Our Approach to ElectroCatalysis Research

Laboratory of ElectroCatalysis, Department of Materials Chemistry

Nejc Hodnik

NATIONAL INSTITUTE OF CHEMISTRY


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Genoa
200 km
Bologna
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BOSNIA AND HERZEGOVINA
Belgrade
Marseille
Nice
Florence
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Sarajevo
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500 km
SPAIN
Barcelona
Mostar
Niš
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MONTE-NEGRO
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MACEDONIA
Valencia
800 km
Tirana
Naples
Salonica
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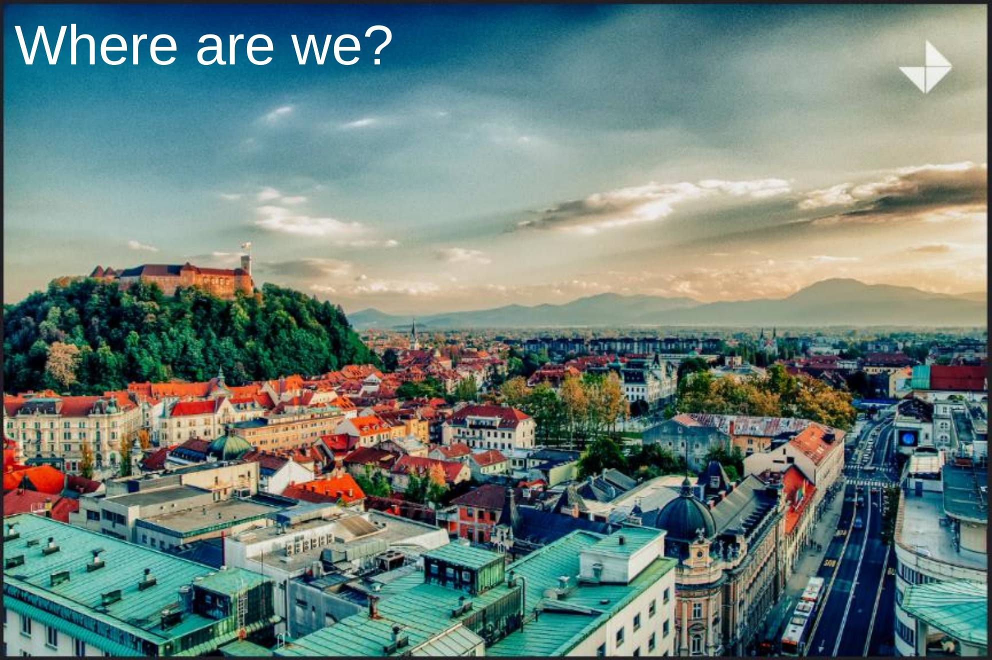
Where are we?



Laboratory of ElectroCatalysis

Department of Materials Chemistry (prof. Gaberšček)

Head (2020 – ERC St. Gr.):

- Assoc. Prof. Nejc Hodnik

Catalyst Synthesis and characterization

- Dr. Marjan Bele
- Dr. Matija Gatalo
- Prof. Miran Gaberšček
- Luka Pavko

Electrosynthesis

- Dr. Primož Jovanovič
- Dr. Vasko Jovanovski

Advanced electrochemical characterization

- Dr. Urša Petek
- Leonard Moriau
- Stefan Popović
- Armin Hrnjić
- Dr. Martin Šala and Dr. Vid Šelh

Electron microscopy

- Prof. Goran Dražič
- Dr. Francisco Ruiz-Zepada
- Gorazd Koderman Podboršek

Recyling

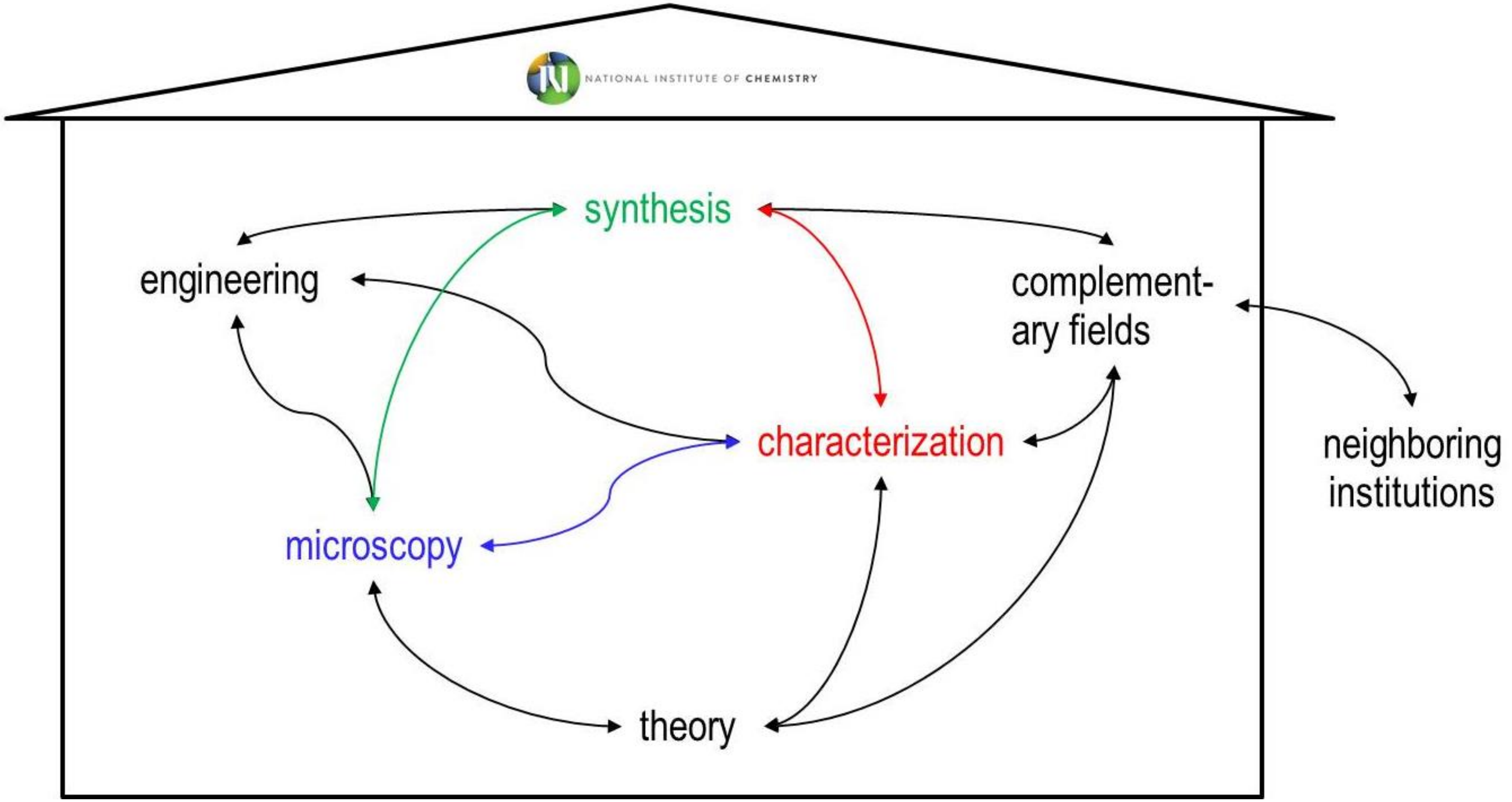
- Dr. Milutin Smiljanic

Collaborations:D13 and D04

Our general approach for materials development

Main goal: try **to understand**

- how materials behave in the synthesis and electrocatalysis

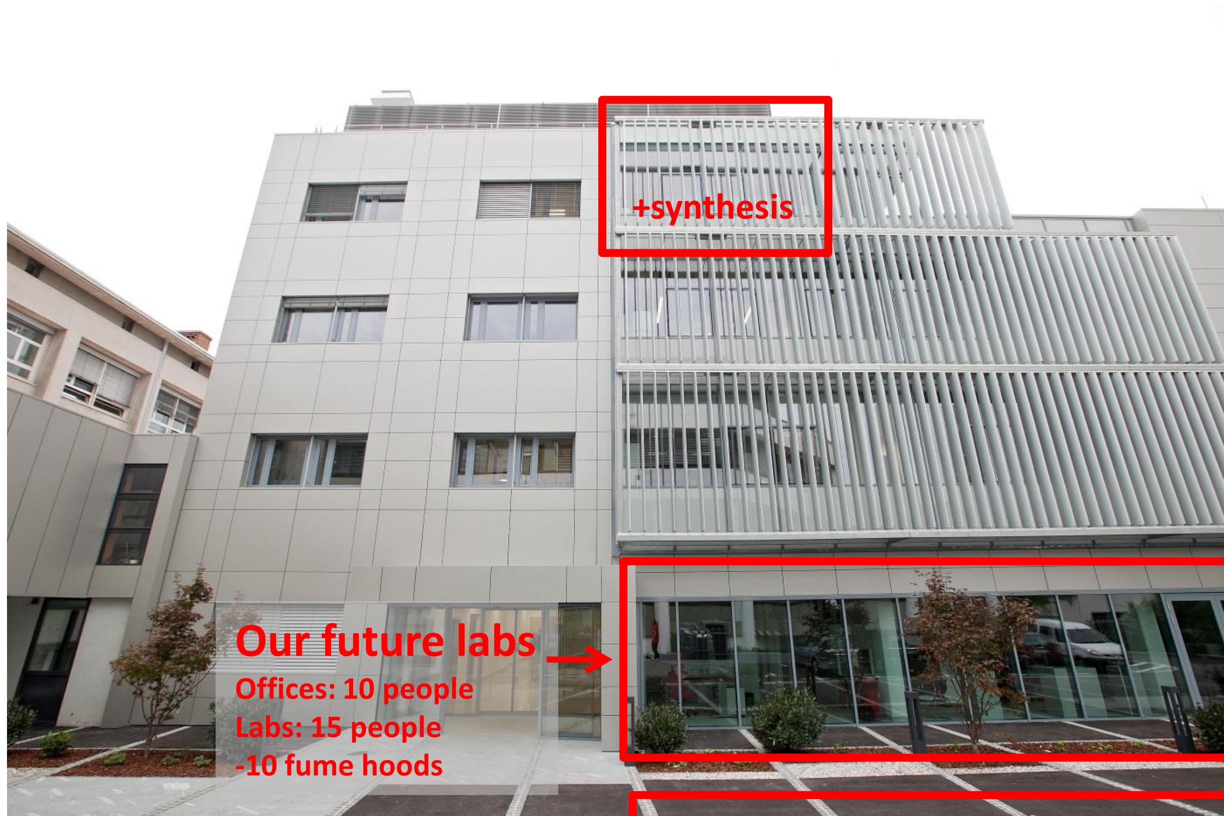


What we can learn from history?

Pregl Research Center
With "high concentration" of analytical instruments

Fritz Pregl
1923 - Nobel Prize

Contributions to quantitative organi cmicroanalysis

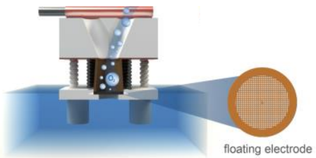


+ TEM & SEM

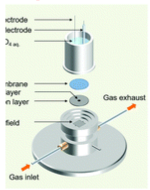
The „machinery“ that we use.

TF-RDE

Floating El.



GDE



GC

HPLC

EFC-ICP-MS

XRD

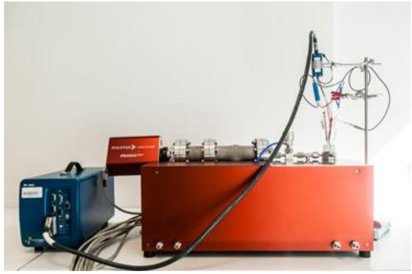
XPS

S/TEM

in-situ holders

SEM, FIB

EC-MS – will have!



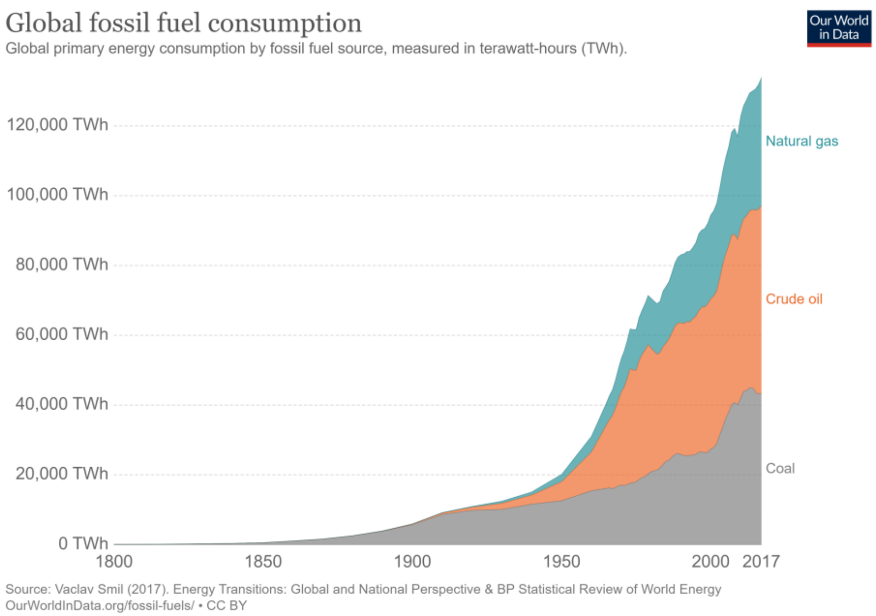
NMR

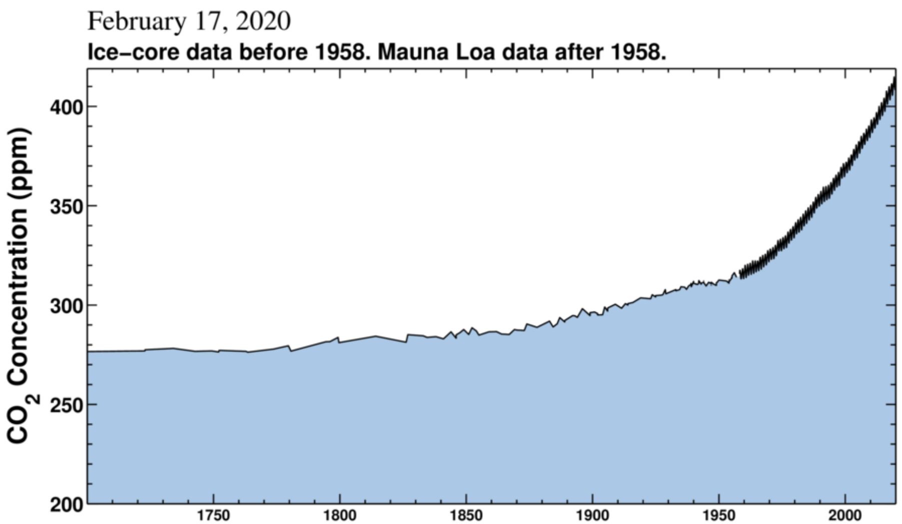
Problem - Global Warming!

We must slow down global worming (below 2 °C) -> rise of greenhouse gas CO_2, that mostly comes from burning of fissile fuels (coil, oil and gas).

„KEELING CURVE“

Pollution





-2016 was the warmest in history
-2019 was the second warmest year and the last five years were the warmest on record
-The average temperature of the last 5 years was between 1.1 and 1.2 °C higher than the pre-industrial level
-Antarctica logs highest temperature on record of 18.3C
-18 out of 19 warmest years were after 2001

https://scripps.ucsd.edu/programs/keelingcurve/

https://climate.copernicus.eu/

http://www3.epa.gov/climatechange/ghgemissions/global.html

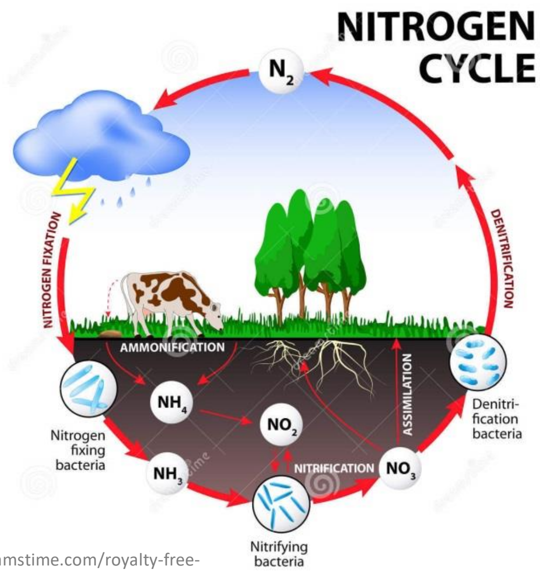
Problems

- **Top Ten Problems of Humanity for Next 50 Years**
- How Noble prize winner Richard Smalley (2003) put it:
  1. **energy**
  2. water
  3. food
  4. envoroment
  5. poverty
  6. terrorism and war
  7. disease
  8. education
  9. democracy
  10. population
      - » 2003 6,3 bilion
      - » 2019 7,7 bilion
      - » 2050 10 bilion

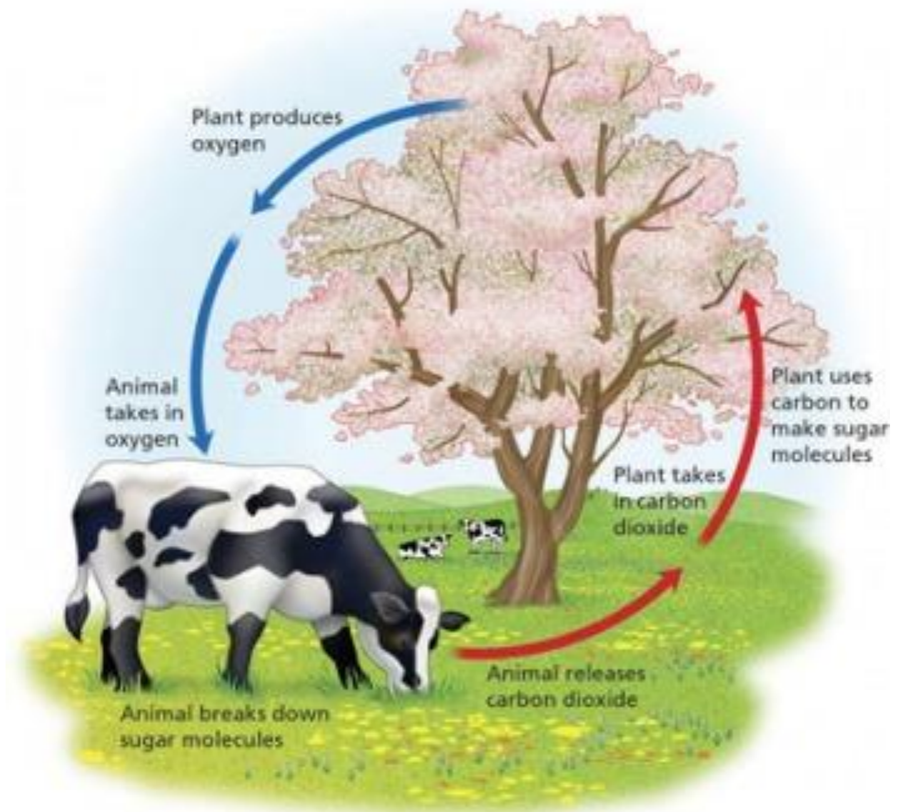
Solutions?

Energy in nature

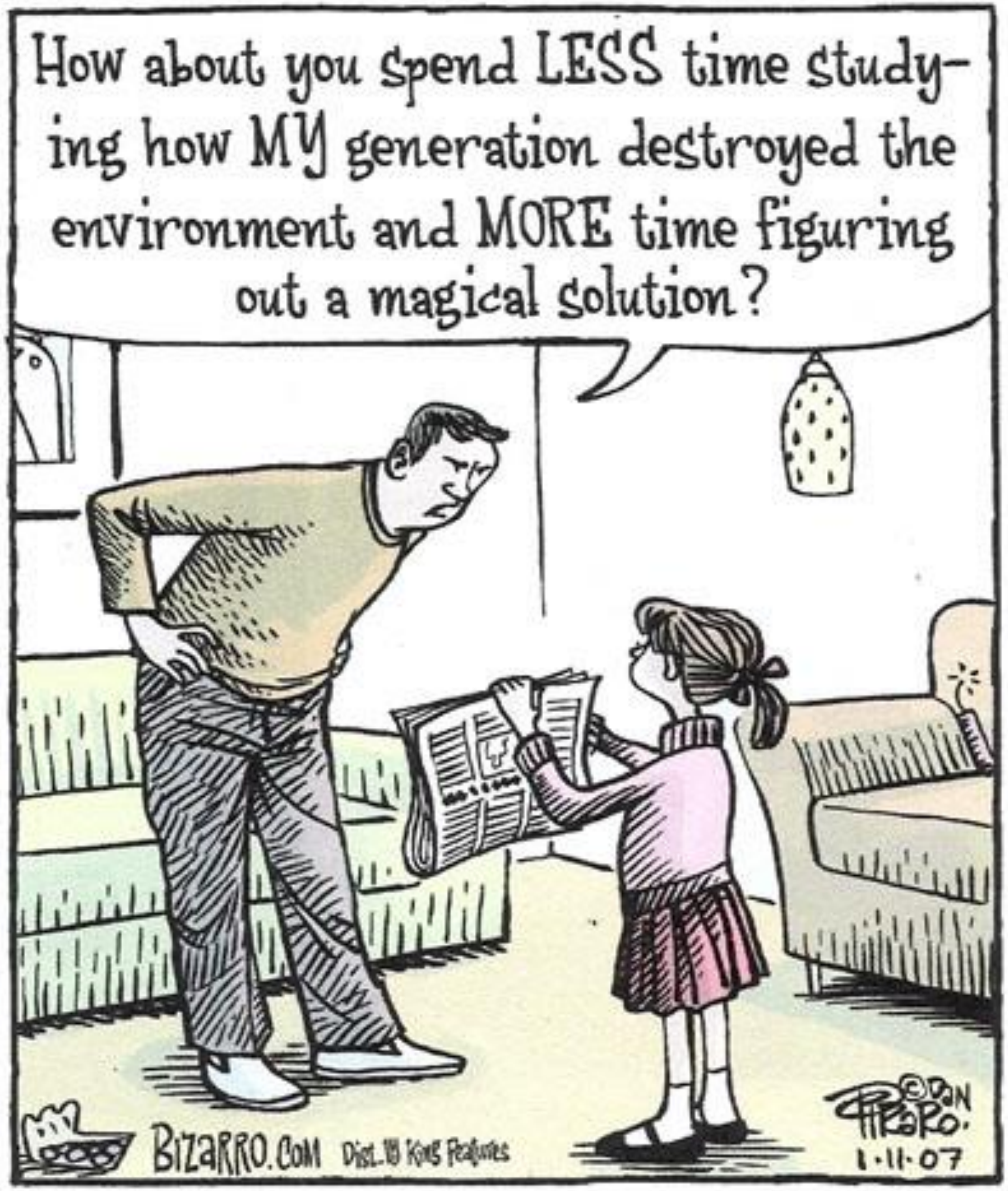
- It stores the energy of the sun, which is the main source of life on earth!
- *via Carbon cycle*
- Slow…



https://www.dreamstime.com/royalty-free-stock-photos-nitrogen-cycle-image29063058



http://ecoregionproject.weebly.com/nitrogen-oxygen-and-carbon-cycles.html


How about you spend LESS time studying how MY generation destroyed the environment and MORE time figuring out a magical solution?
BIZARRO.COM Dist. by King Features
© DAN PIRARO. 1-11-07

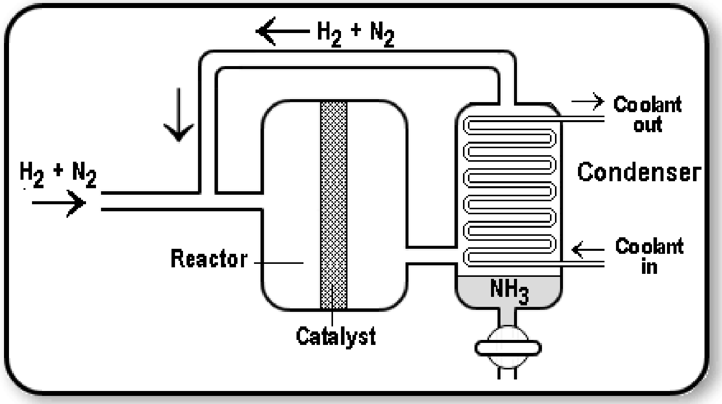
Solutions?

What did we do?

- Example from history: **Haber–Bosch process** (1910)**:**
- is an artificial nitrogen fixation (*nitrogen cycle*) process and is the main industrial procedure for the production of ammonia today
- The process converts atmospheric **nitrogen** (**N_2**) to ammonia (NH_3) by a reaction with **hydrogen** (**H_2**) using a metal catalyst under high temperatures and pressures
- Before the Haber process, ammonia had been difficult to produce on an industrial scale; Grand Challenge.

Fritz Haber
1919 - Nobel Prize

https://en.m.wikipedia.org/wiki/Haber_process



https://chemstuff.co.uk/academic-work/a-level/the-haber-process/

Solutions?

What did we do?

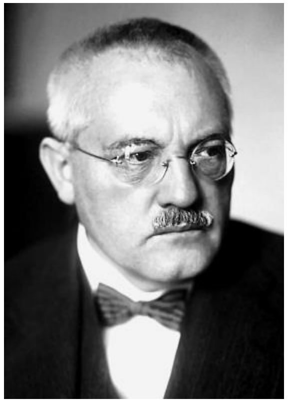
- Example from history: **Bergius process** (1913)**:**
- is a method of production of **liquid synthetic fuel** by catalytic hydrogenation of high-volatile bituminous coal at high temperature and pressure. („*partial“ carbon cycle*)
- Before the Bergius process, liquid fuel like diesel oil or petrolium was difficult to get, especially in Germany; Grand Challenge.

Fredrich Bergius
1931 - Nobel Prize

https://en.m.wikipedia.org/wiki/Haber_process

- The Fischer–Tropsch process (1925) is collection of chemical reactions that converts a mixture of **carbon monoxid** (**CO**) and **hydrogen** (H_2) **into liquid hydrocarbons - fuel**. („*partial“ carbon cycle*)

Carl Bosch
1931 - Nobel Prize



Solutions?

What can we do?

- As scientists, we can find new ways to store and distribute solar energy, which are sustainable and more efficient.
- This is mainly to reduce dependencies on fossil fuels by reducing them (in addition to pollution)
  - For example, the conversion of biomass or CO_2 into chemicals or fuel
- The sun, in less than an hour, gives us enough energy for the whole year

https://landartgenerator.org/blagi/archives/127

- **Current big challenges:**

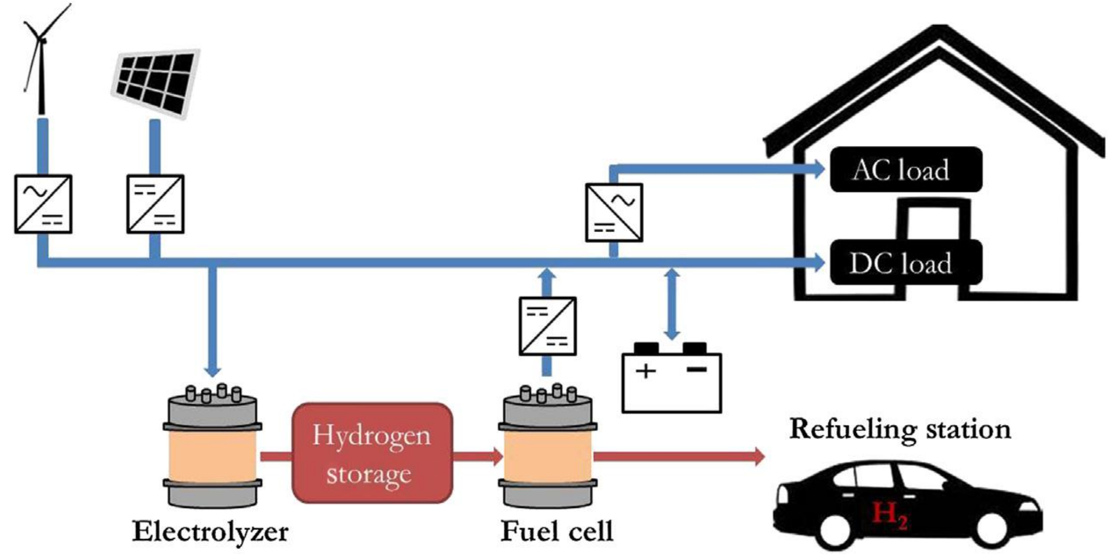
energy storage (night!) & catalytic conversion

Solutions?

What about hydrogen economy?

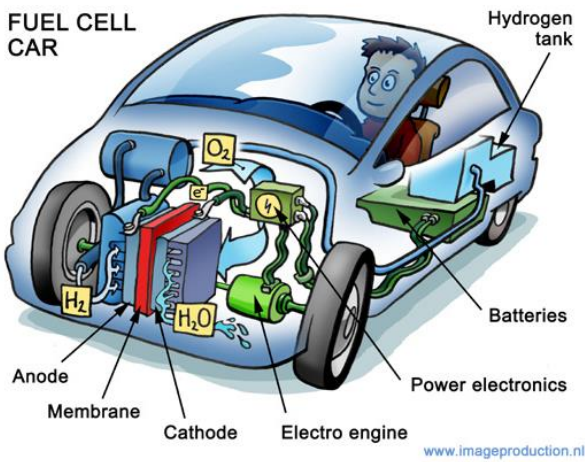
John O'M Bockris, 1972!

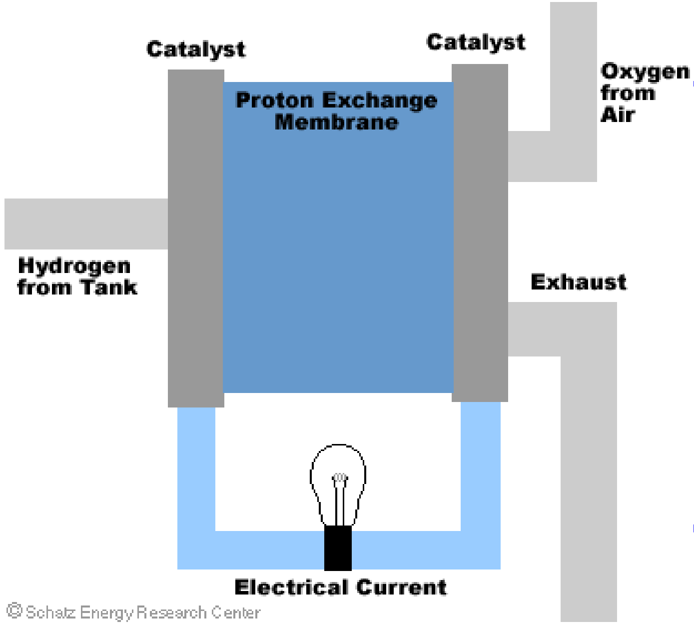
- We store solar (wind) energy in hydrogen, which is an energy vector.
- Hydrogen cycle:



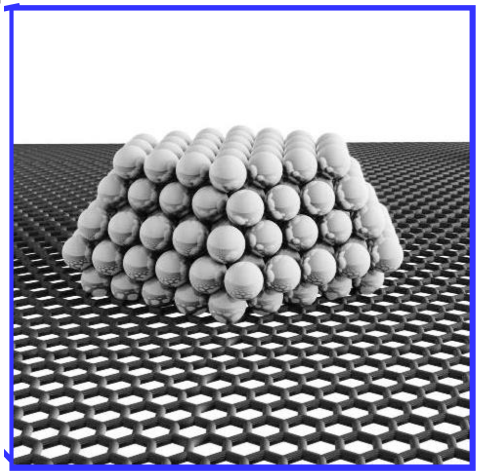
Proton exchange membrane fuel cell

No emissions – no CO_2! Only $2H_2 + O_2 \rightarrow 2H_2O$





Electrocatalysts are Pt-based nanoparticles on high surface carbon.



PEM-FC electrocatalyst stil requires improvement of performance & stability & cost !
Most promising are Pt-alloys. It is important to study their electrochemical behaveour – their stability!

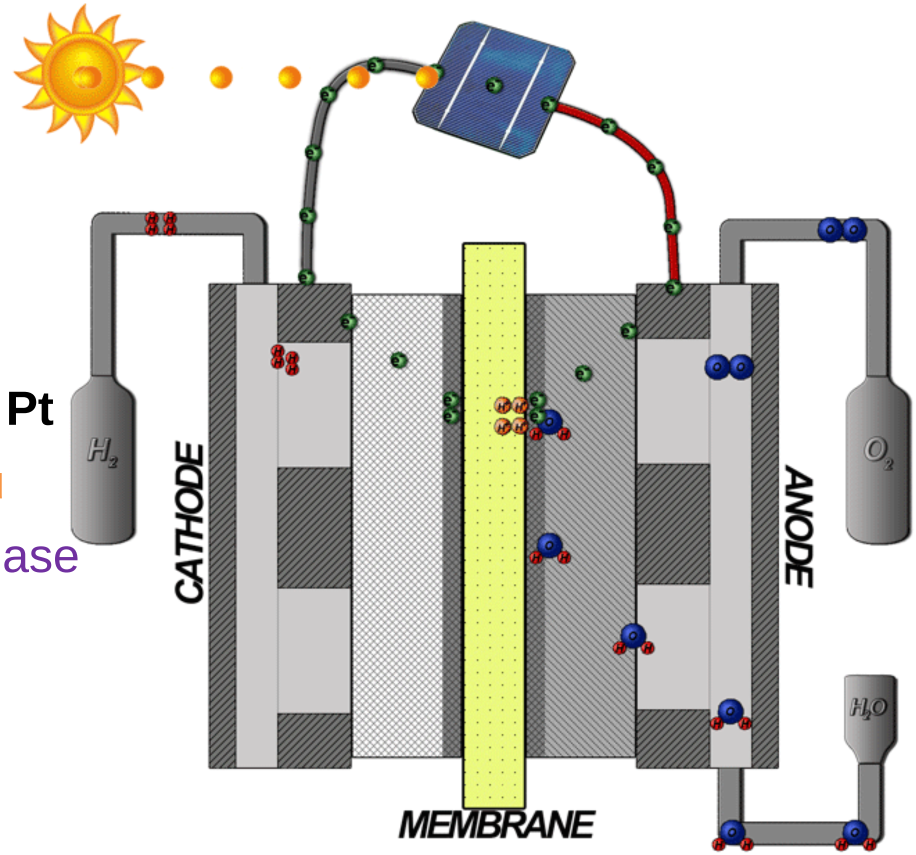
Proton exchange membrane electrolyzer

No emissions – no CO_2! Only $2H_2O \rightarrow 2H_2 + O_2$

Hydrogen evolution - **Pt**

CO_2 redcution - **Cu**

N_2 redcution - nitrogenase



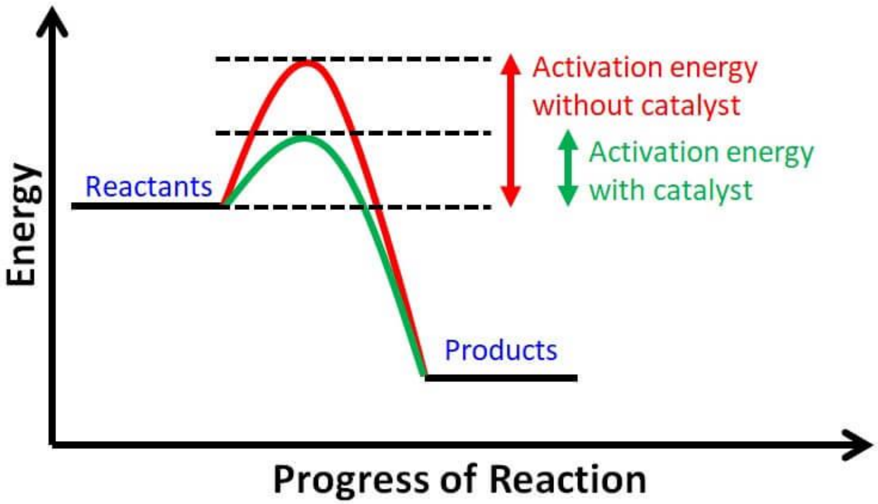
Oxygen evolution –

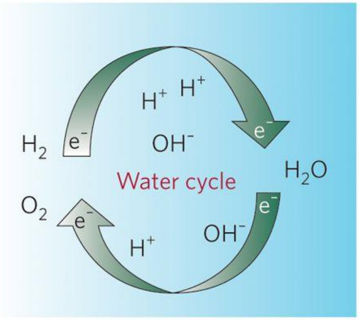
Ir and Ru?

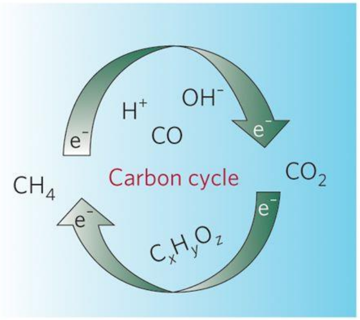
PEM-EL electrocatalyst stil requires improvement of performance & stability & cost !
Most promising are Ir- and Ru-based alloys. It is important to study their electrochemical behaveour stability!

What is a catalyst?

- It is a substance that enables or accelerates a chemical reaction without being consumed.
- A good catalyst makes us use less energy to make a product.







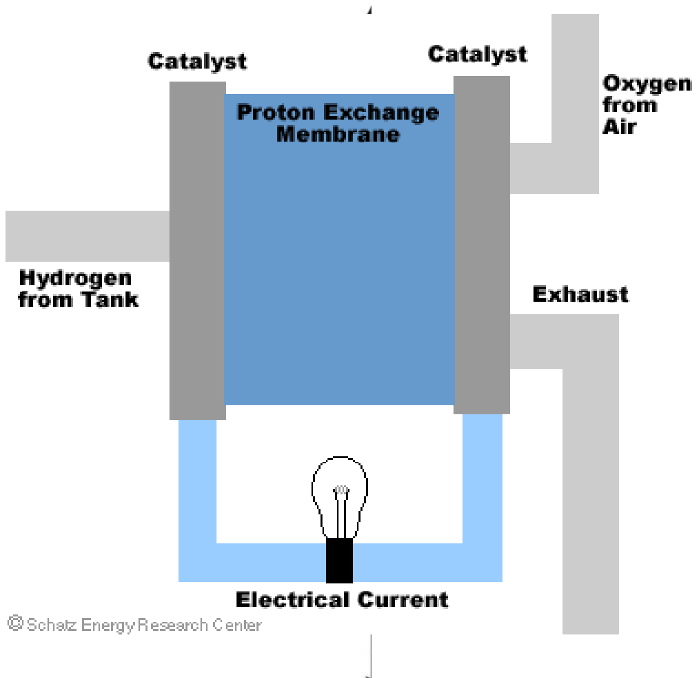
https://www.fuelcellstore.com/fuel-cell-components/catalyst

Why electrocatalysis?

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

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

Main difference is the double layer! Old field…reinvigorated!

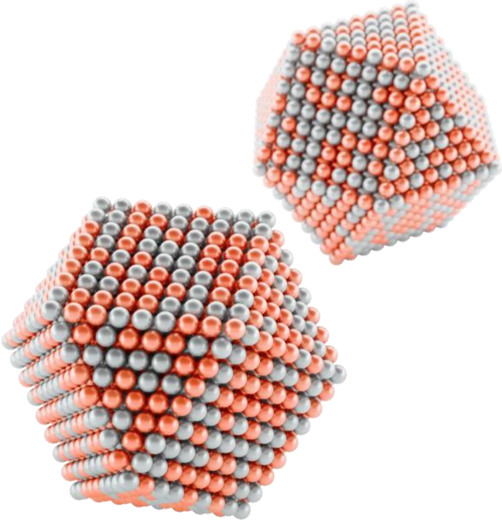


It has relevance to the future possibilities of the energy infrastructure!

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

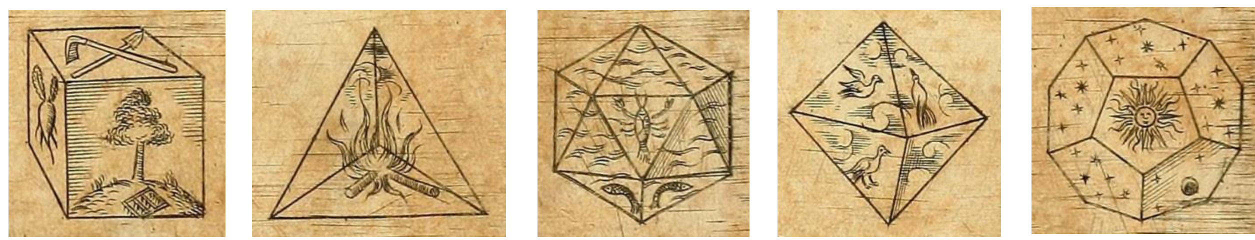
What are nanoparticles

- 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 300 – 5000, 4 nm pa 20000 atoms
- Nanozymes
- Electrocatalysts

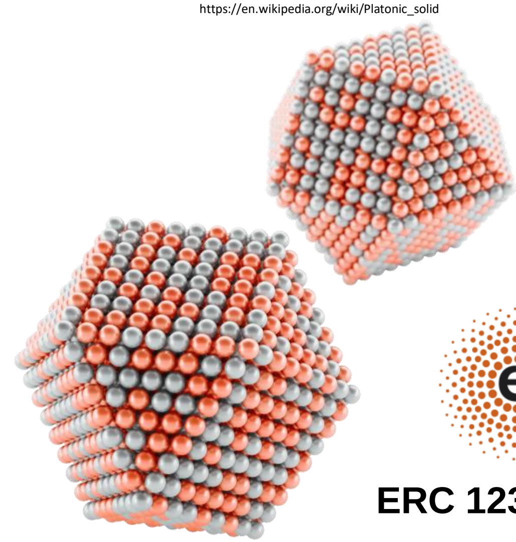


Shape of (nano) particle is perfect

- Perfection, as predicted by Plato, unfortunately does not exist in the world. In practice, no nanoparticle has the perfect geometric shape of the polyhedron
- Platonic bodies:

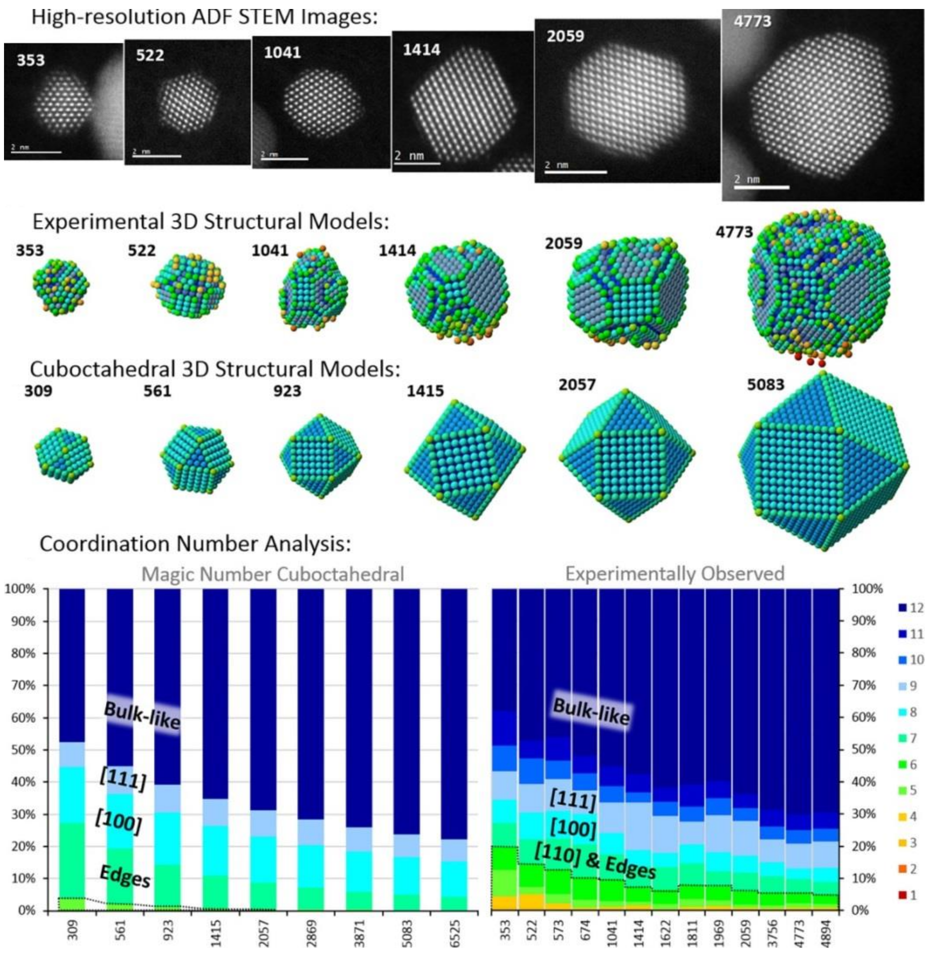


https://en.wikipedia.org/wiki/Platonic_solid

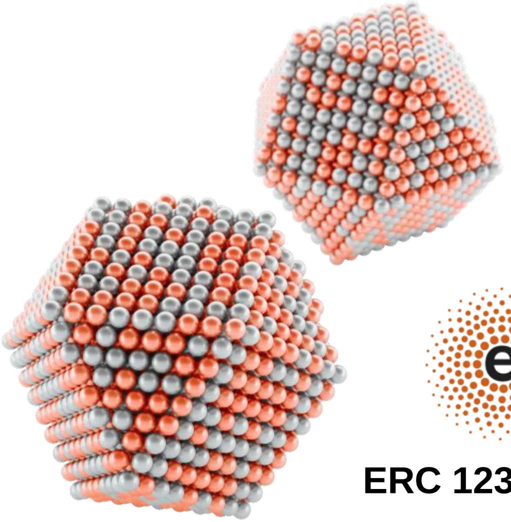


ERC 123STABLE

No (nano) particle is perfect



No two particles that we will examine will be alike!

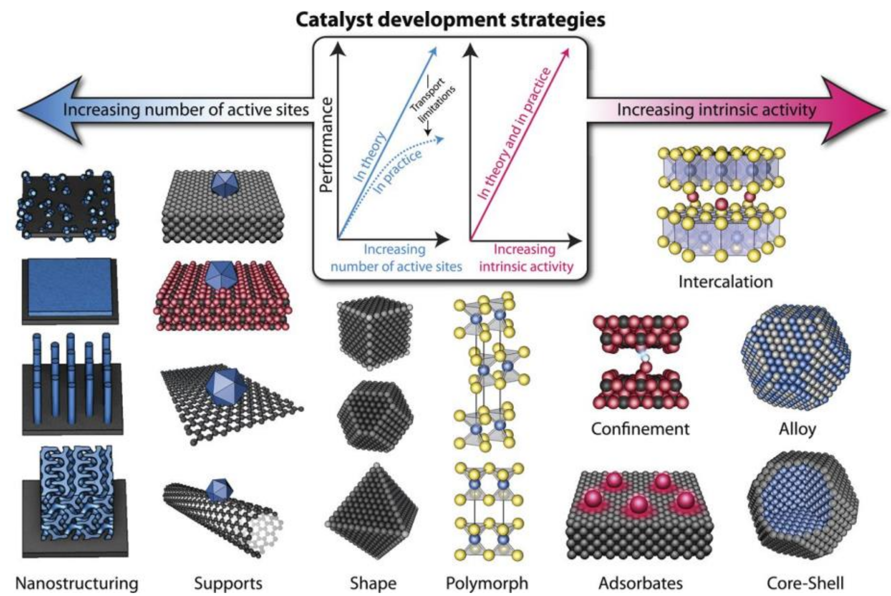


ERC 123STABLE

What defines metal electrocatalyst activity?

e.g. PEM Fuel Cell (Pt) or Electrolyzer (Ir)

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



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

Practically everything we can think of!

NATURE CATALYSIS PERSPECTIVE

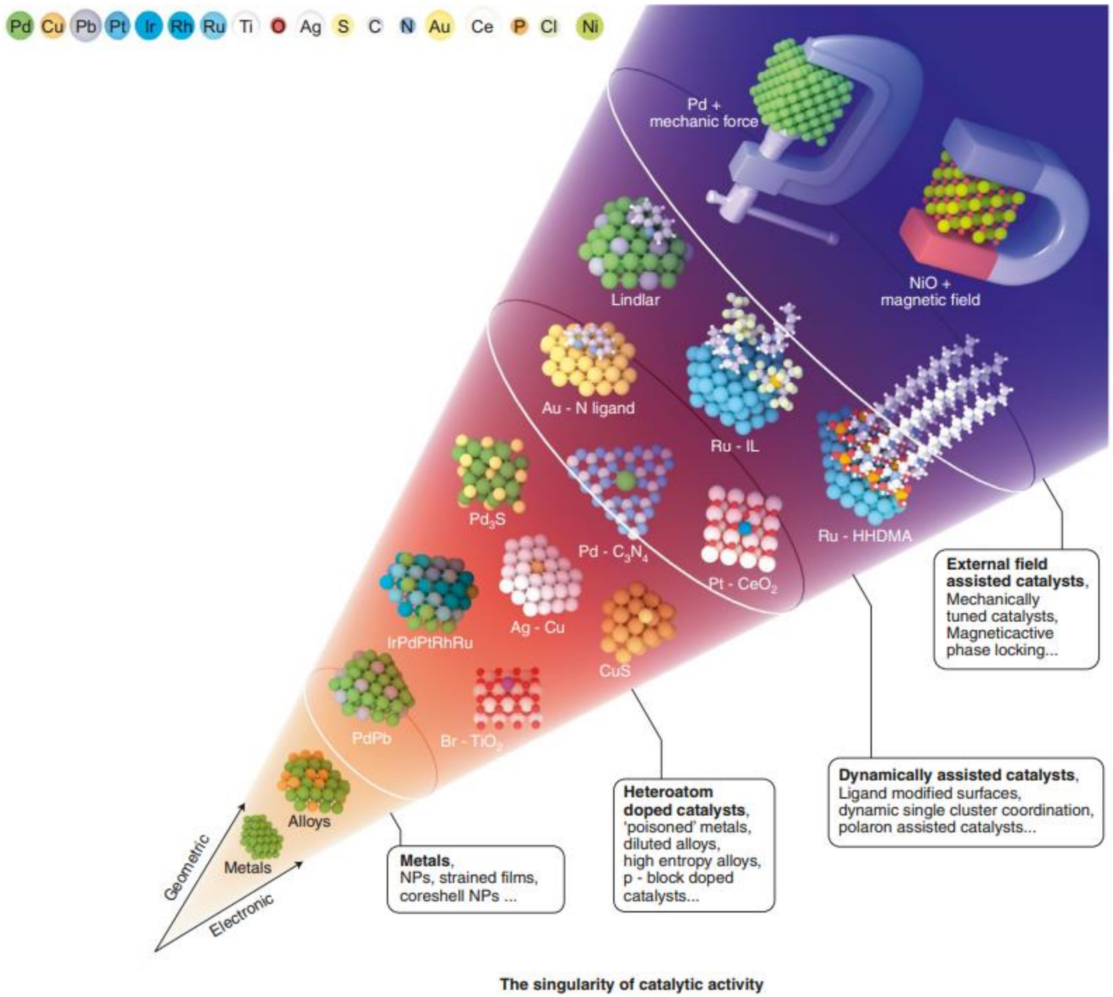
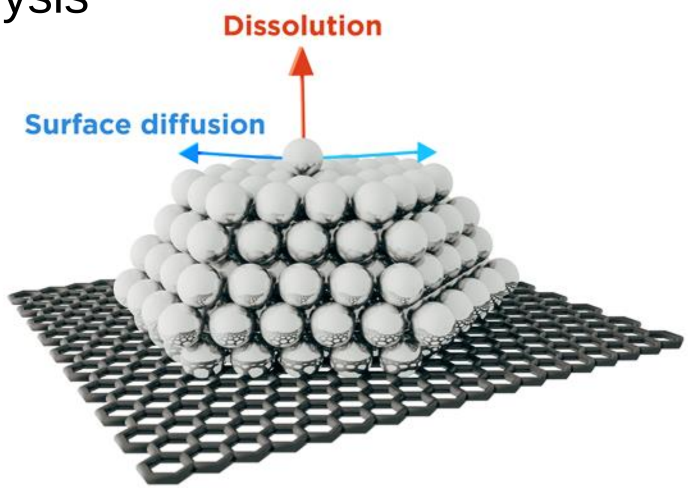


Fig. 2 | The cone timeline of breaking linear-scaling relationships strategies. Structures are placed according to their mostly electronic or mostly geometric contributions. The identified rules can be described in terms of complexity (diagonal timeline). The lowest design level corresponds to metal-only systems and simple alloys and the changes induced by strain[26] or coordination. The second level is formed by doped systems: metal-in-metal single atoms[27], high entropy alloys[39], self-doped semiconductors[41], p-doped systems[53]. The third complexity level encompasses ligand modified systems[42], organometallic systems[59], single atoms in carbon matrixes[30] and their dynamic electronic and geometric effects[56]. The highest level corresponds to the introduction of external forces[62–64], such as light, mechanic or magnetic forces.

Performance of catalysts

- Activity
- Stability
- Selectivity

Structure-activity-selectivity relationship on atomic level can be considered as a **state-of-the-art** in (electro)catalysis

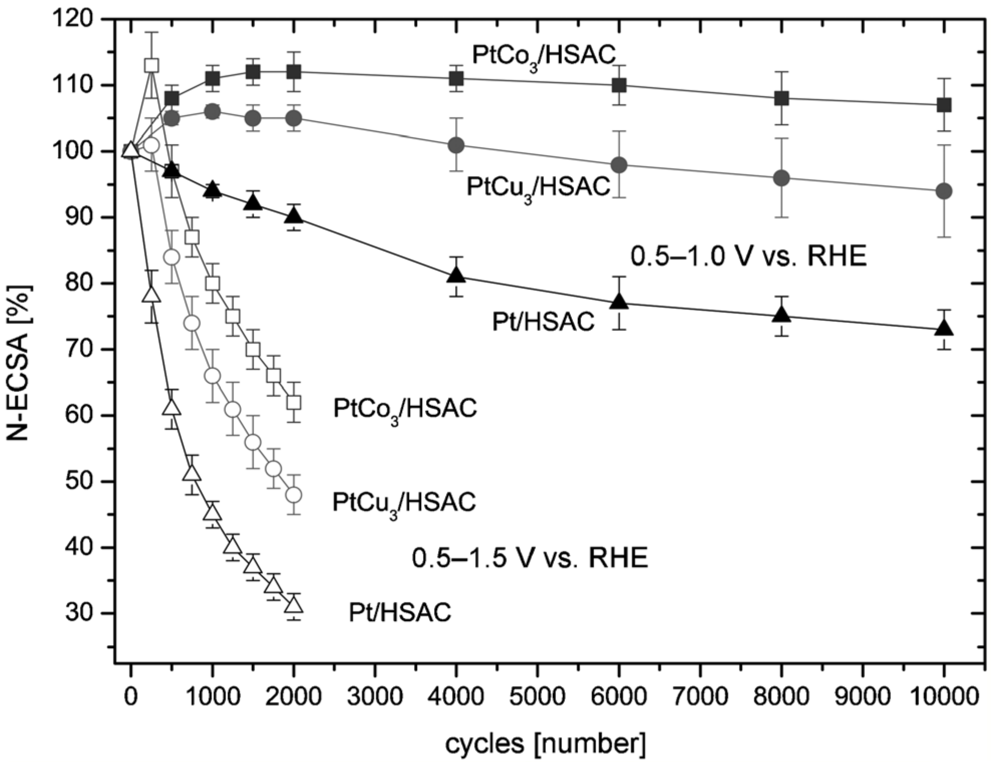


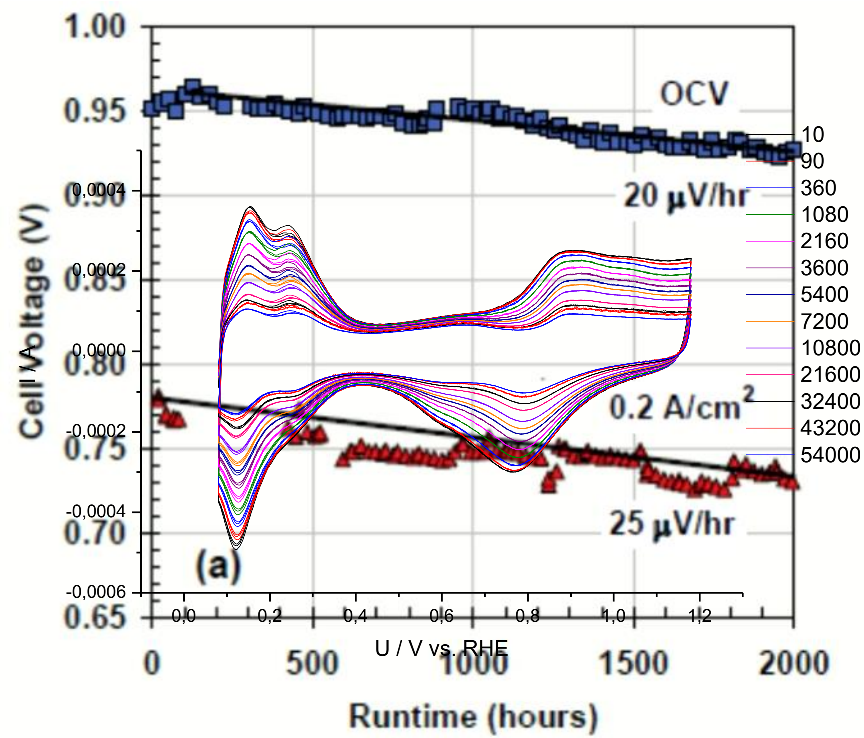
Structure-stability relationship at the atomic level is much less explored

Examples of our approaches

- Degradation of Pt-based fuel cell catalysts
- Degradation of Ir-based electrolyzer catalysts?
- Degradation of Cu-based CO_2RR catalysts

Proton exchange membrane fuel cell





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

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

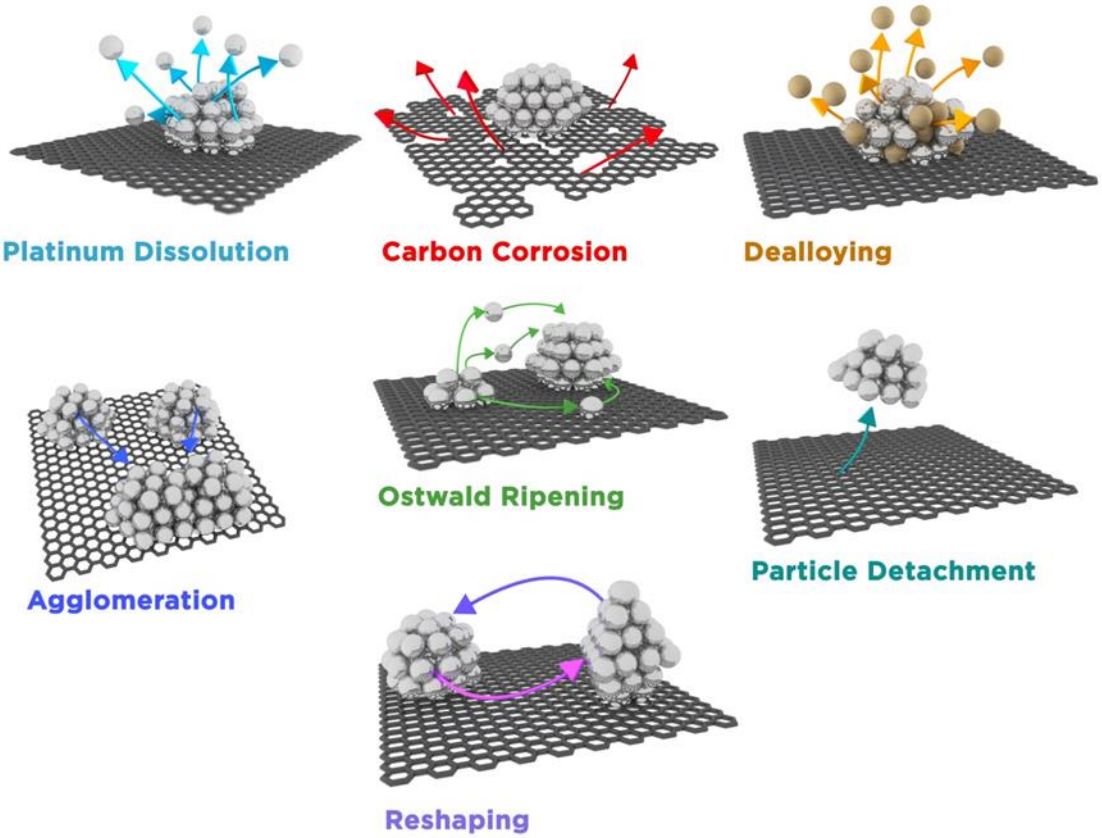
Is it possible to avoid this – we must truly understand fundamentals first –> ex-situ tests

Degradation of Pt-based fuel cell catalyst

Mechanisms for the loss of active surface area:

Most studies performed on Pt or PGM at low pH – Fuel Cell.

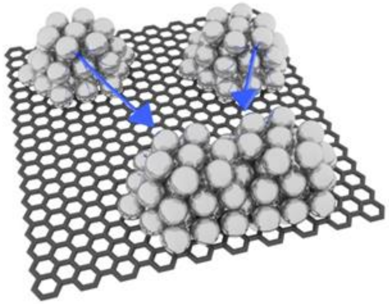
Degradation at oxidative potentials!



Degradation of Pt-based fuel cell catalyst

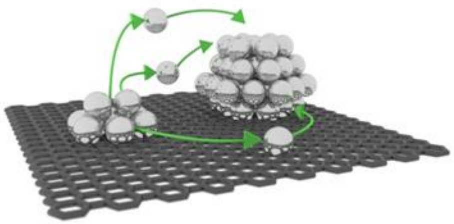
Postmortem analysis?
No!

How to distinguish between them?

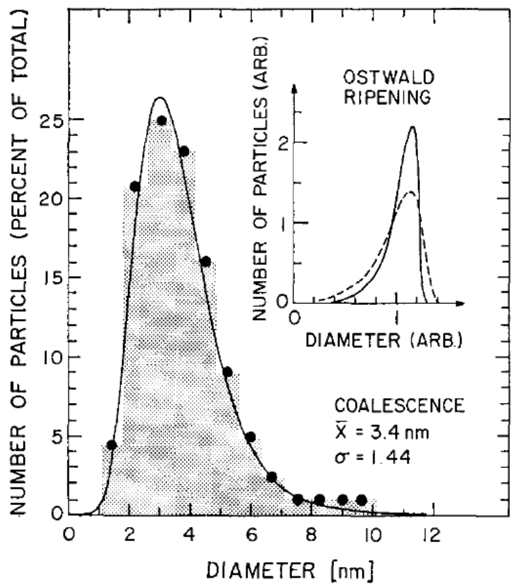


Agglomeration

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**.



Ostwald Ripening



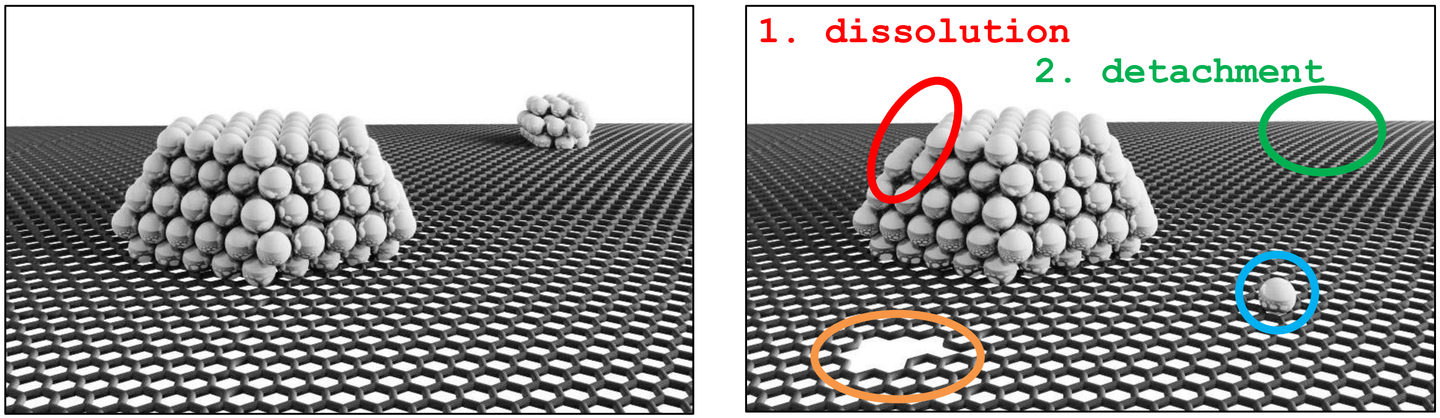
Problem: the simple models assume that only one growth mode occurs! – not true!

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

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

One of our approaches - as a game

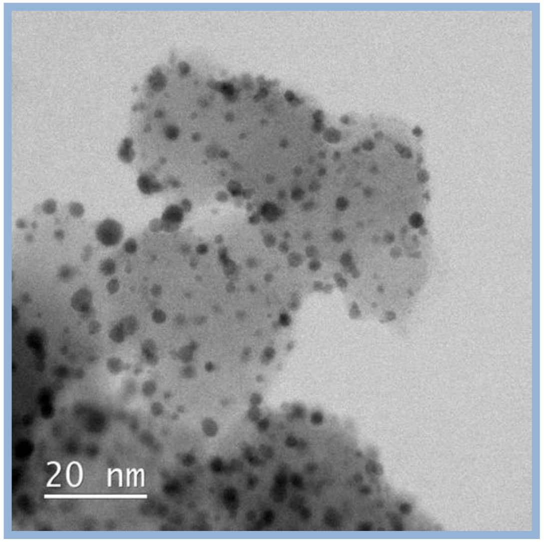
Find the four differences between the two electrocatalyst images before and after aging - and then mark on the other.



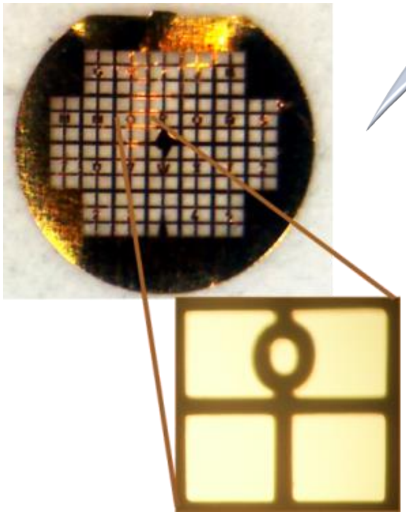
- since the history of the physical properties of the site is known, reliable conclusions can be drawn about very complex restructuring events such as degradation mechanisms

Simple principle: *Look at the grid in the TEM, take it out and perform the electrochemistry, and again look at the grid in the TEM!*

Electrochemical cell



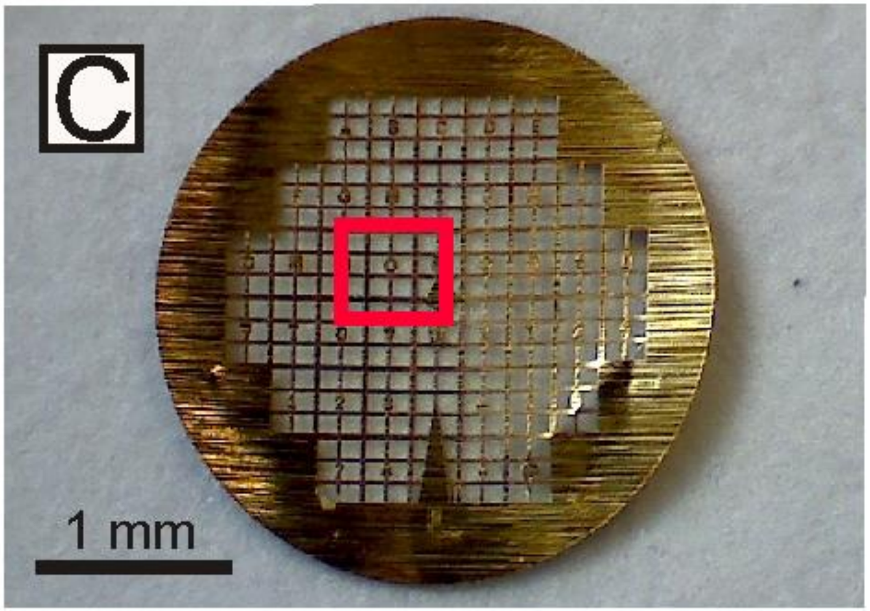
The Gold finder TEM grid allows to retrieve the same spot throughout the electrochemical treatments.

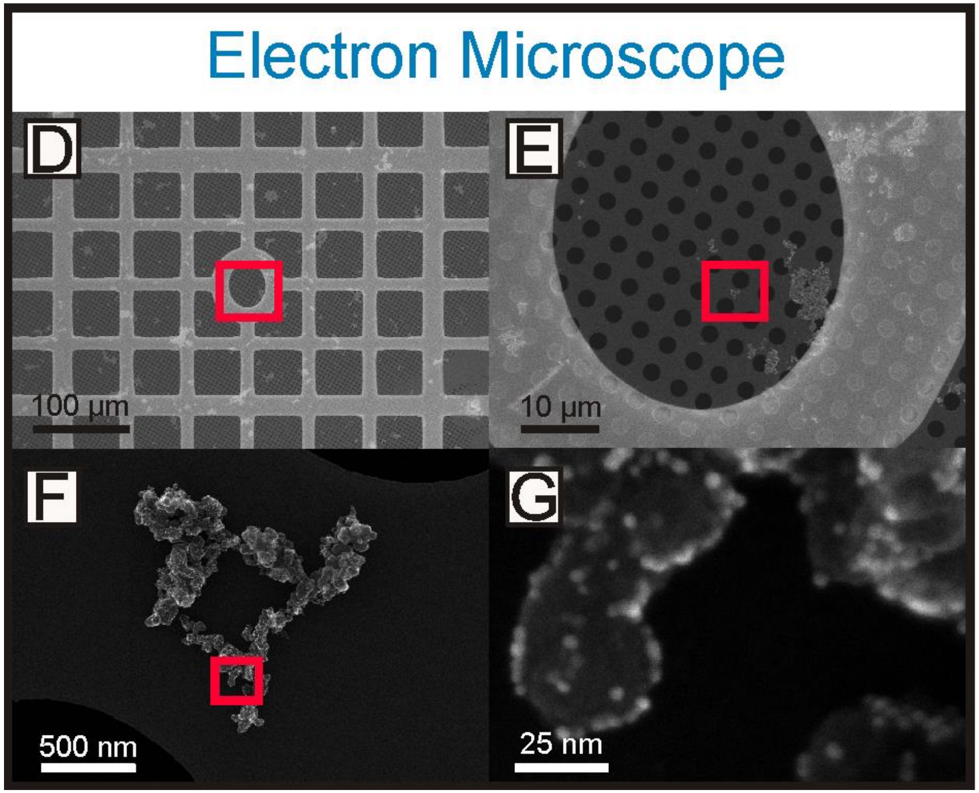


Atomic resolution STEM - JEOL ARM 200 CF

Such approach has been proven extremely usefull in providing a direct link between macroscopic and microscopic behavior

Mayrhofer, K., et al; *Electrochem. Commun.* **2008**, 10, 1144-1147.





- Utilizing a TEM finder grid as a WE
  - Conducting, but inert Au

- Tracking of the catalyst particles
  - Alphanumerical signs for orientation

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

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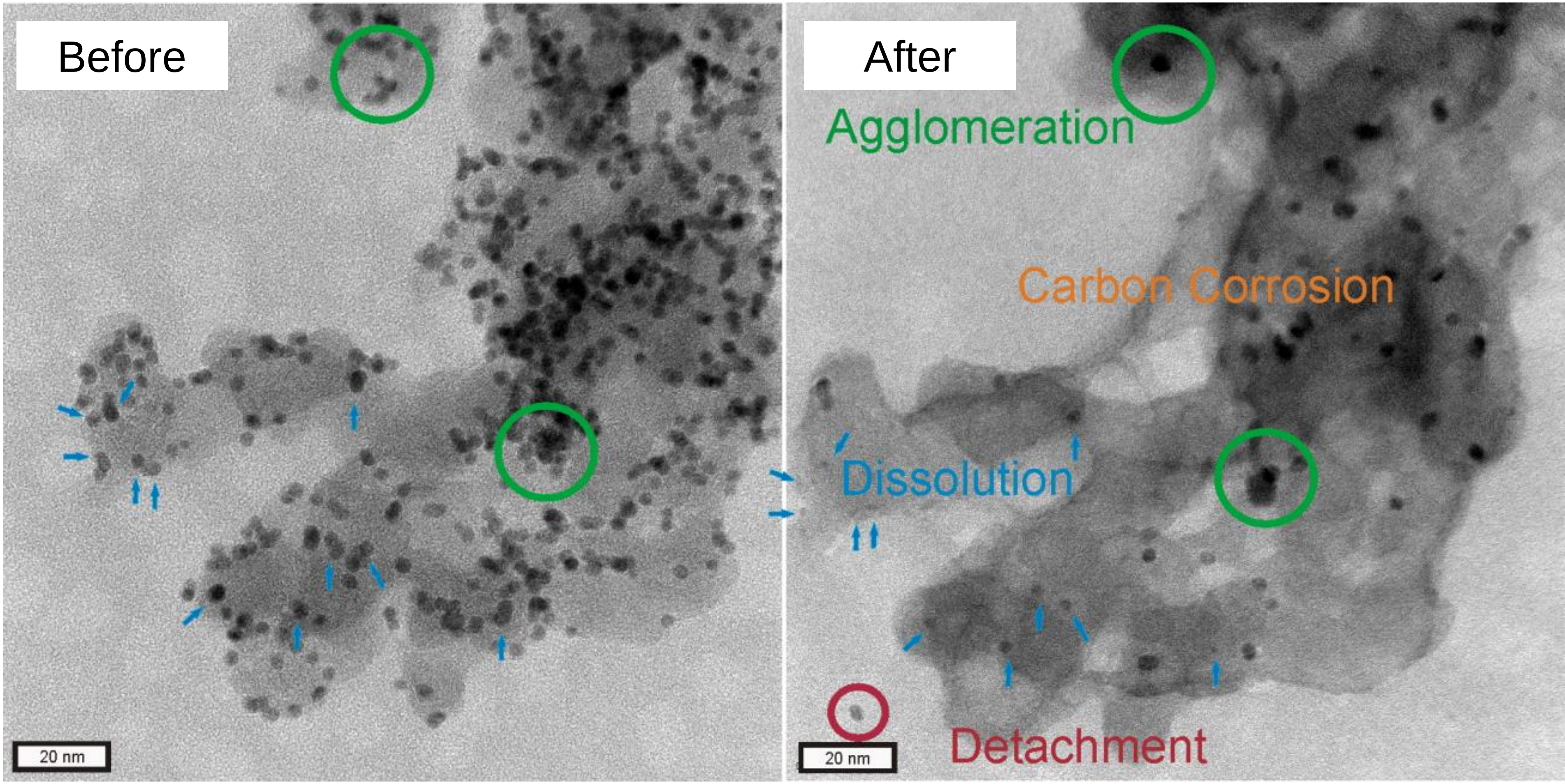
Pt/Vulcan
(20 wt.%, 3.6 nm)

Overlapping degradation mechanisms – material dependant

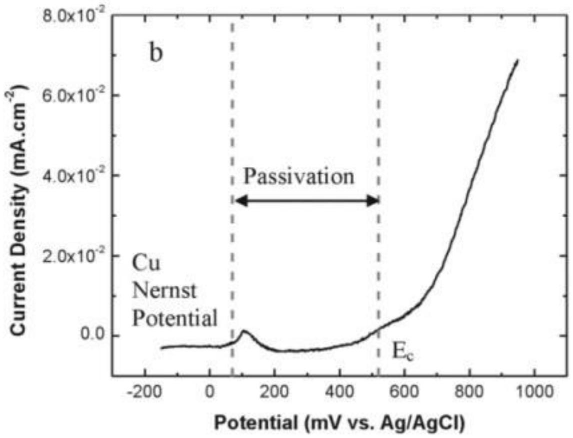


3600 potential cycles, 0.4 – 1.4 V_{RHE}, 0.1 M $HClO_4$, 1 Vs^{-1}

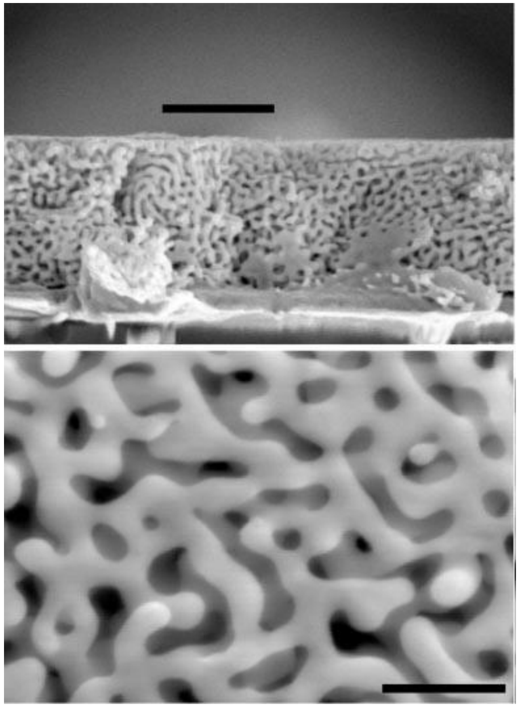
Meier, *ACS Catalysis,* **2012**, 2, 832-843.

Dealloying is selective removal of less noble metal.

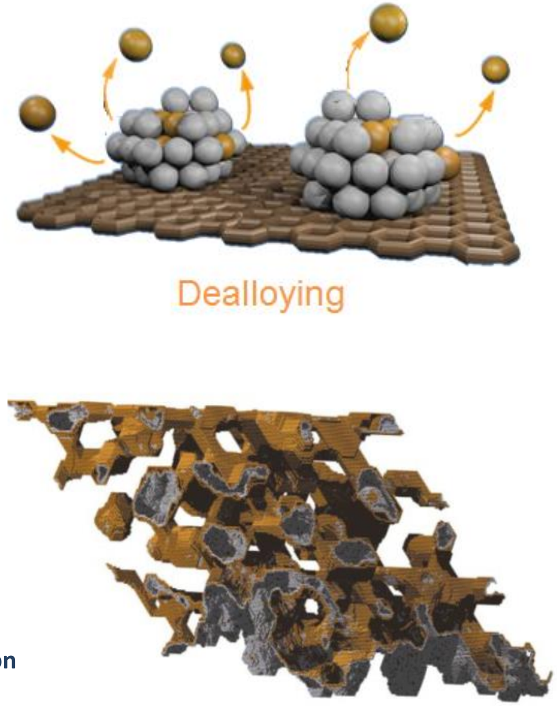
”It is a competition between surface diffusion of noble metal (Pt) and tendency of less noble metal (Cu) to dissolve



R. Yang et al, J. Phys. Chem. C 115 (2011) 9074–9080.



–> pore formation

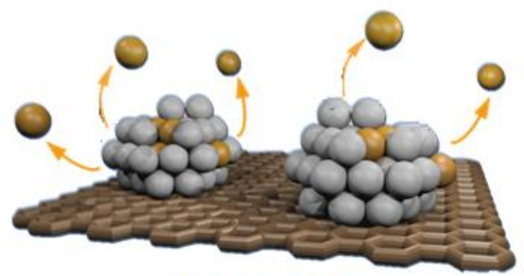


J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, and K. Sieradzki, Nature (London) 410, 450 (2001).

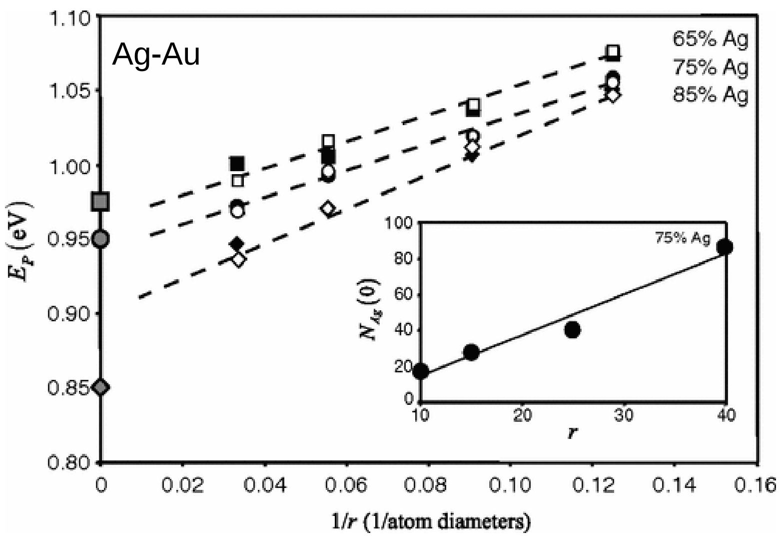
Dealloying is particle size dependant!

The Gibbs-Thomson effect:

with 1/r there is increased mobility of surface atoms, the surface of the particle quickly passivates



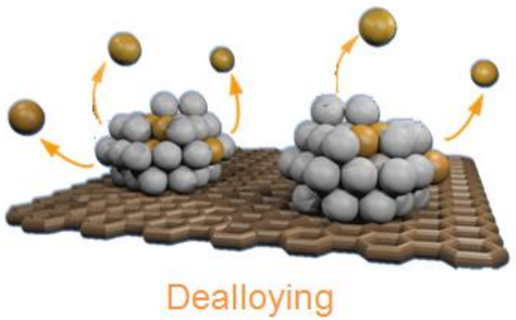
Model:



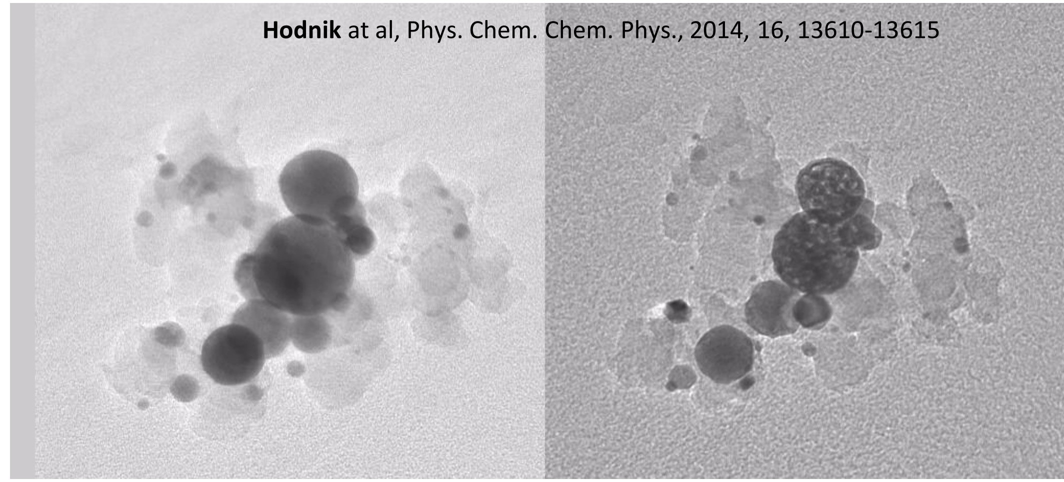
Simulation and model data for the potential for porosity evolution E_P versus of 1/r.

I. McCue, J. Snyder, X. Li, Q. Chen, K. Sieradzki, and J. Erlebacher Phys. Rev. Lett. 108, 225503 – Published 31 May 2012

Pot. Hold @ 1.2 V $PtCu_3$



Hodnik* et al. *PCCP* (**2014**) 16(27), pp. 13610-13615

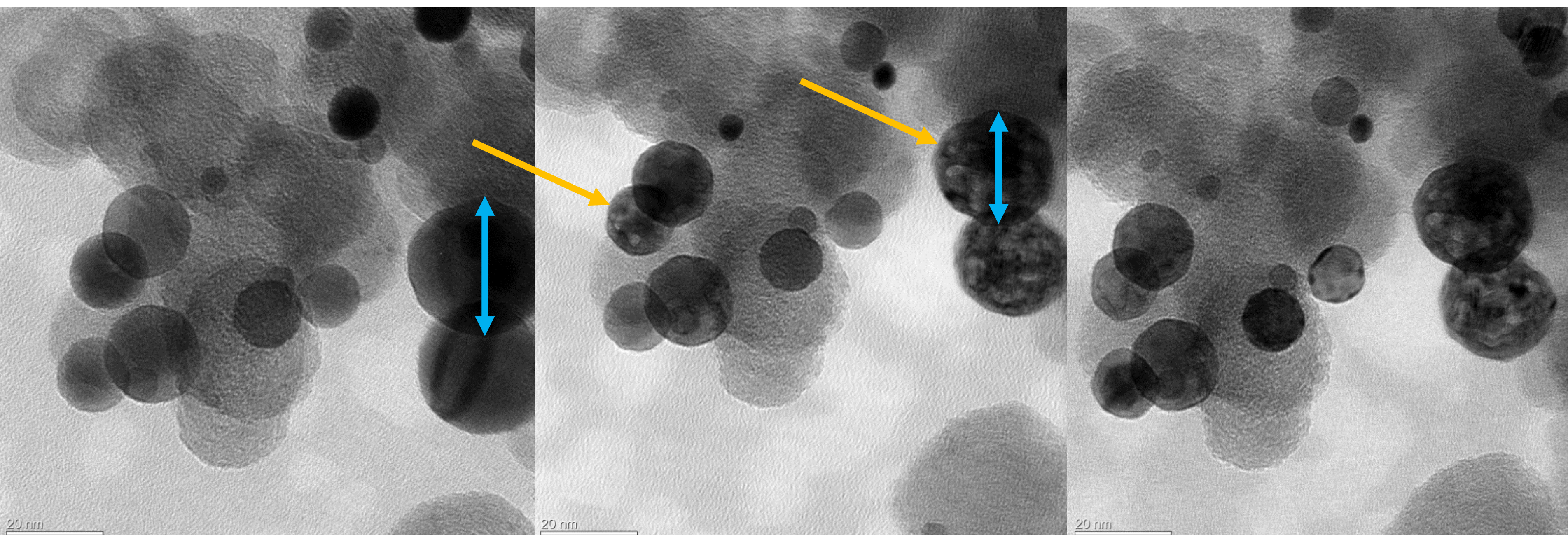


Before dealloying

~50-75 % of Cu removed

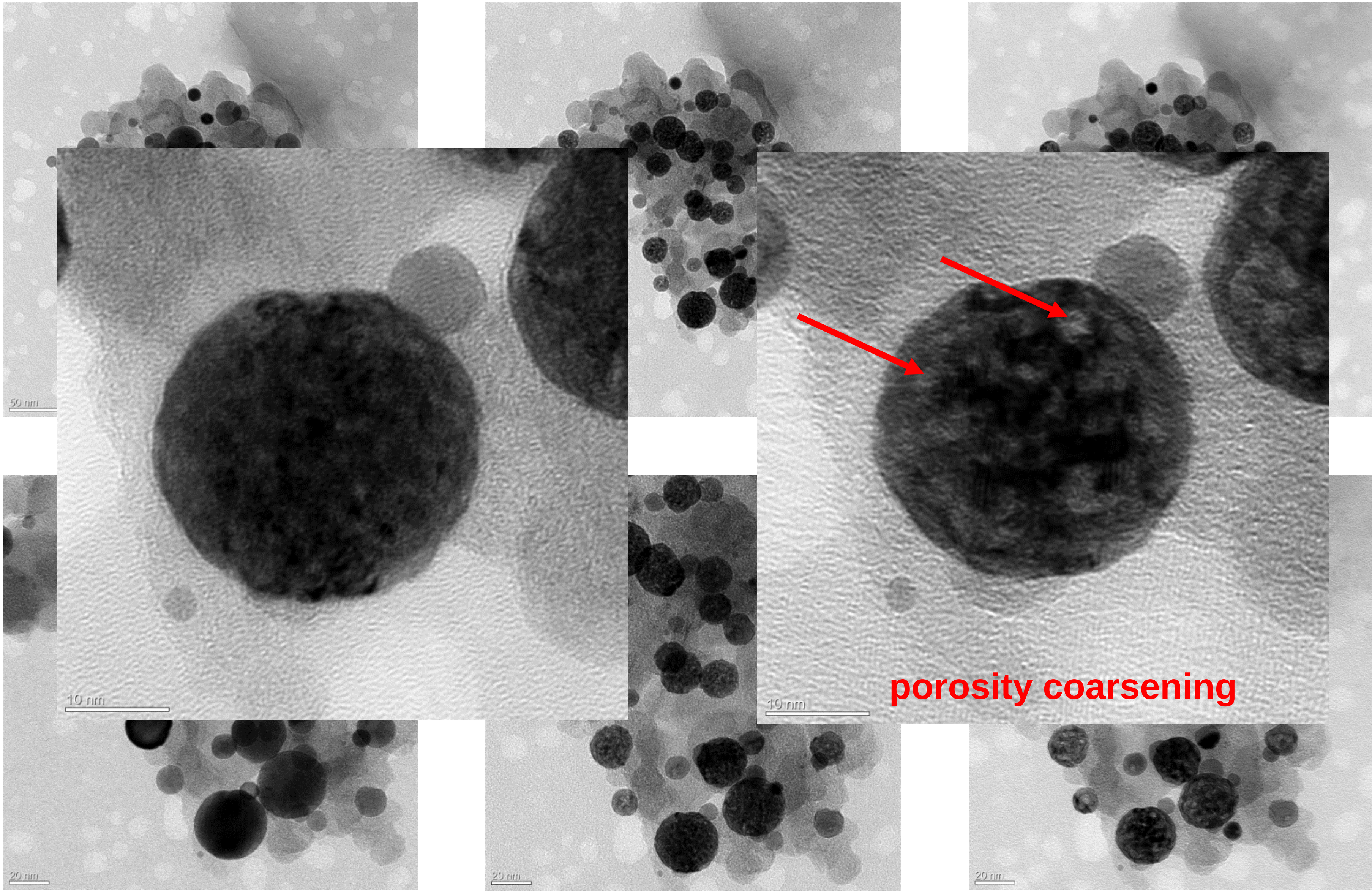
Hold at 1.2V for 2 Hrs

Cycling: 0.6 to 1.2 V,
scan rate=1 V/s; 7000 cycles

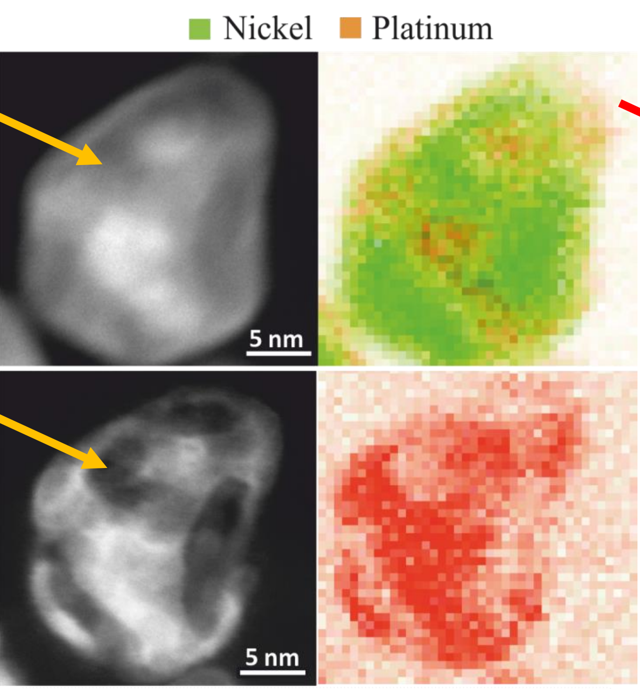


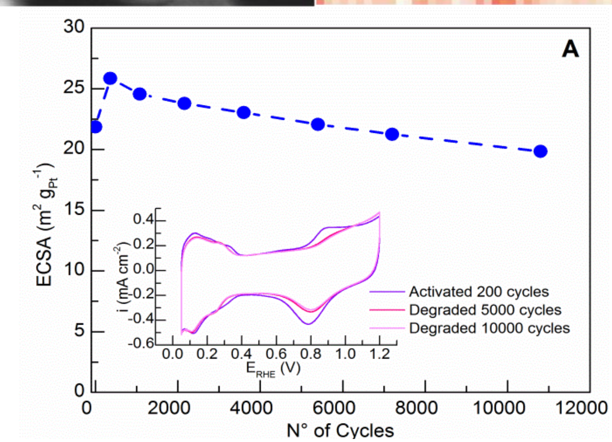
Jeyabharathi at al, ChemCatChem 2013, 5, 2627 – 2635

Univerza v Novi Gorici, Dvorec Lanthieri, 20.2.2020

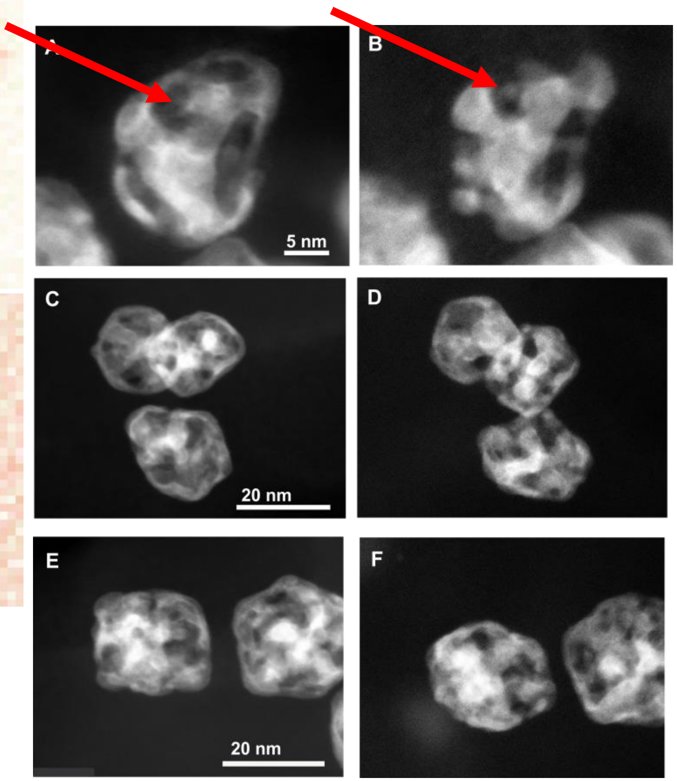


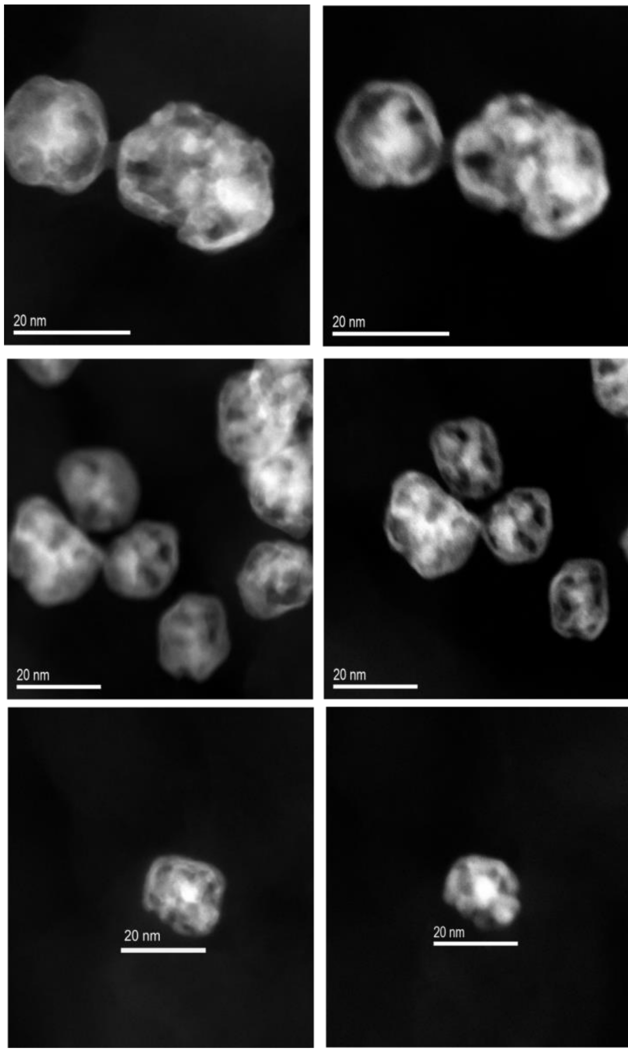
dealloying





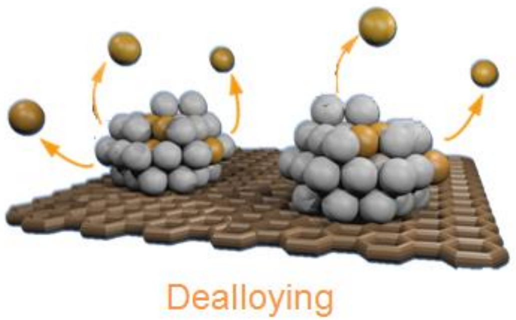
porosity coarsening



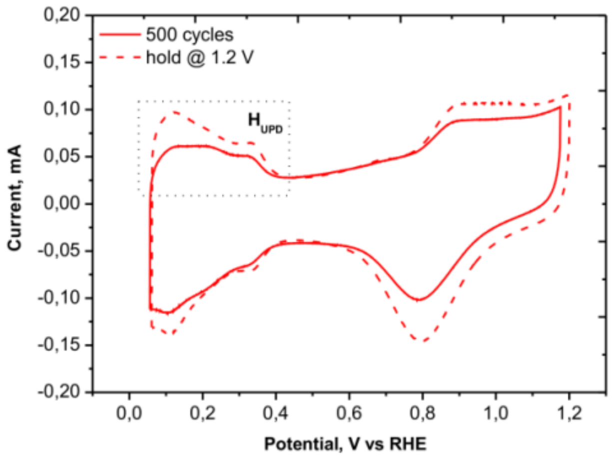


Baldizzone, *ACS Catal.*, **2015**, *5*, 5000–5007

Cyc. Up to 1.2 V $PtCu_3$



Hodnik* et al. *PCCP* (**2014**) 16(27), pp. 13610-13615

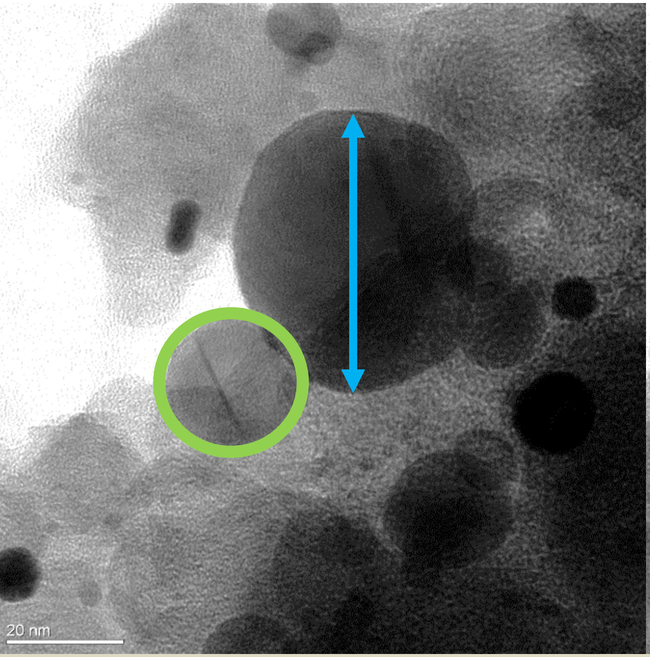


- -Cubo Octahedron
- -Truncated Octahedron
- -Cube
- -Tetrahexahedral

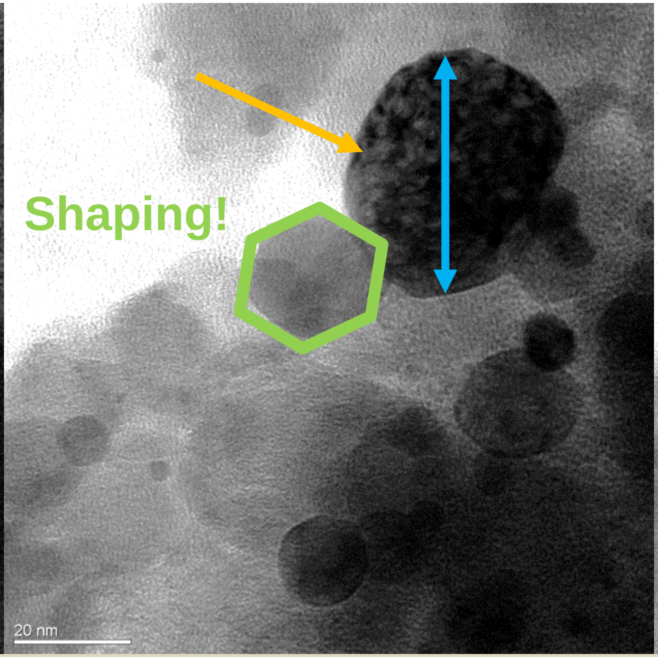
Na Tian*, et al Science* **316**, 732 (2007)

–0.10 and –0.20 V to 1.20 V vs. SCE

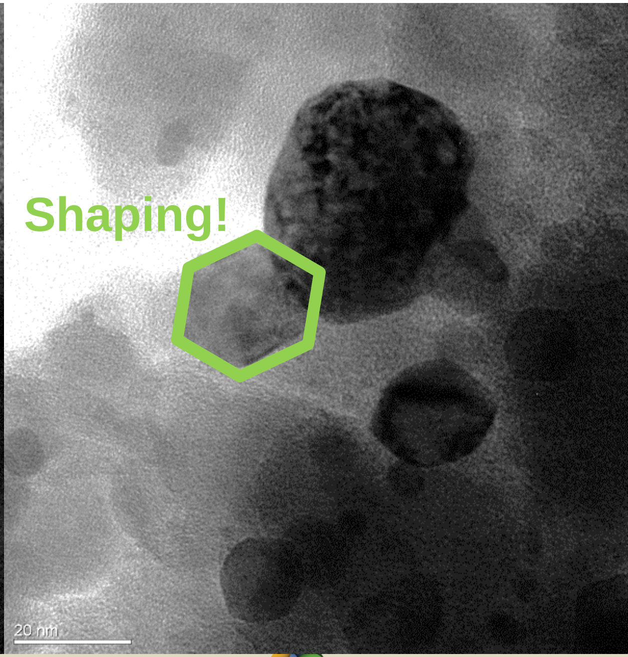
Before dealloying



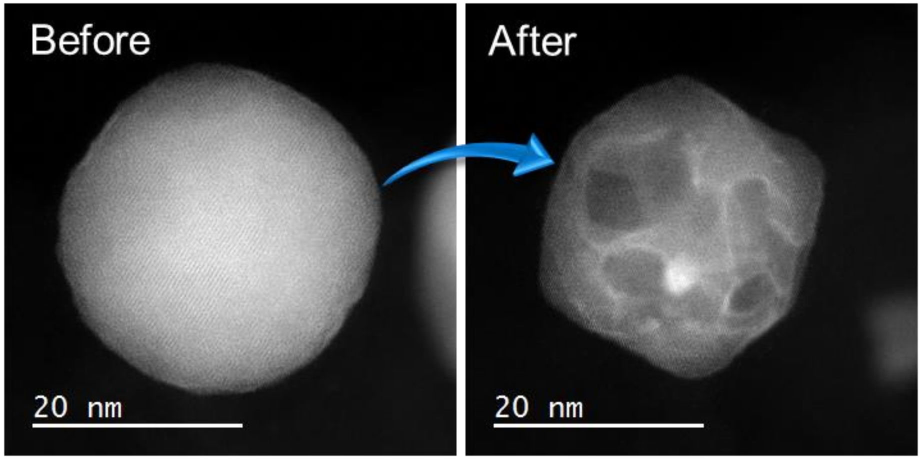
Cycling: 0.05 to 1.2 V, scan rate=0.5 V/s; 500 cycles (2 Hrs)

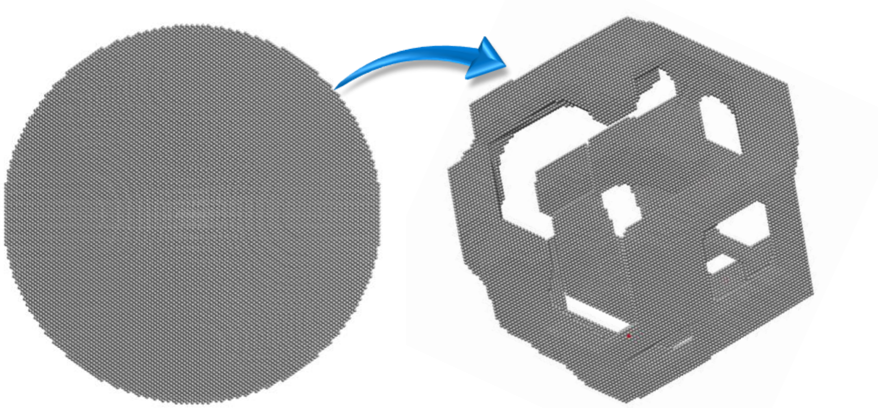


Cycling: 0.6 to 1.2 V, scan rate=1 V/s; 7000 cycles



$PtCu_3$ dealloying – selective Cu dissolution

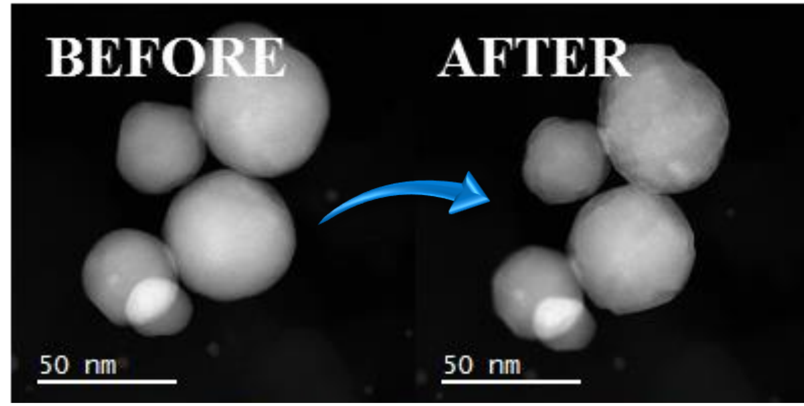


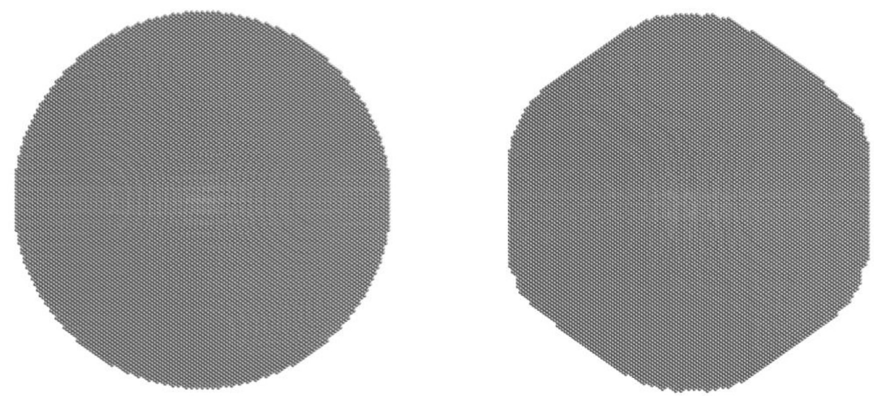


Multi-scale process Monte Carlo & micro-kinetics modeling of deallyoing process and mass transport

Pavlišič, ACS Catal., 2016, 6 (8), pp 5530–5534
Zepeda, ChemCatChem, 2017

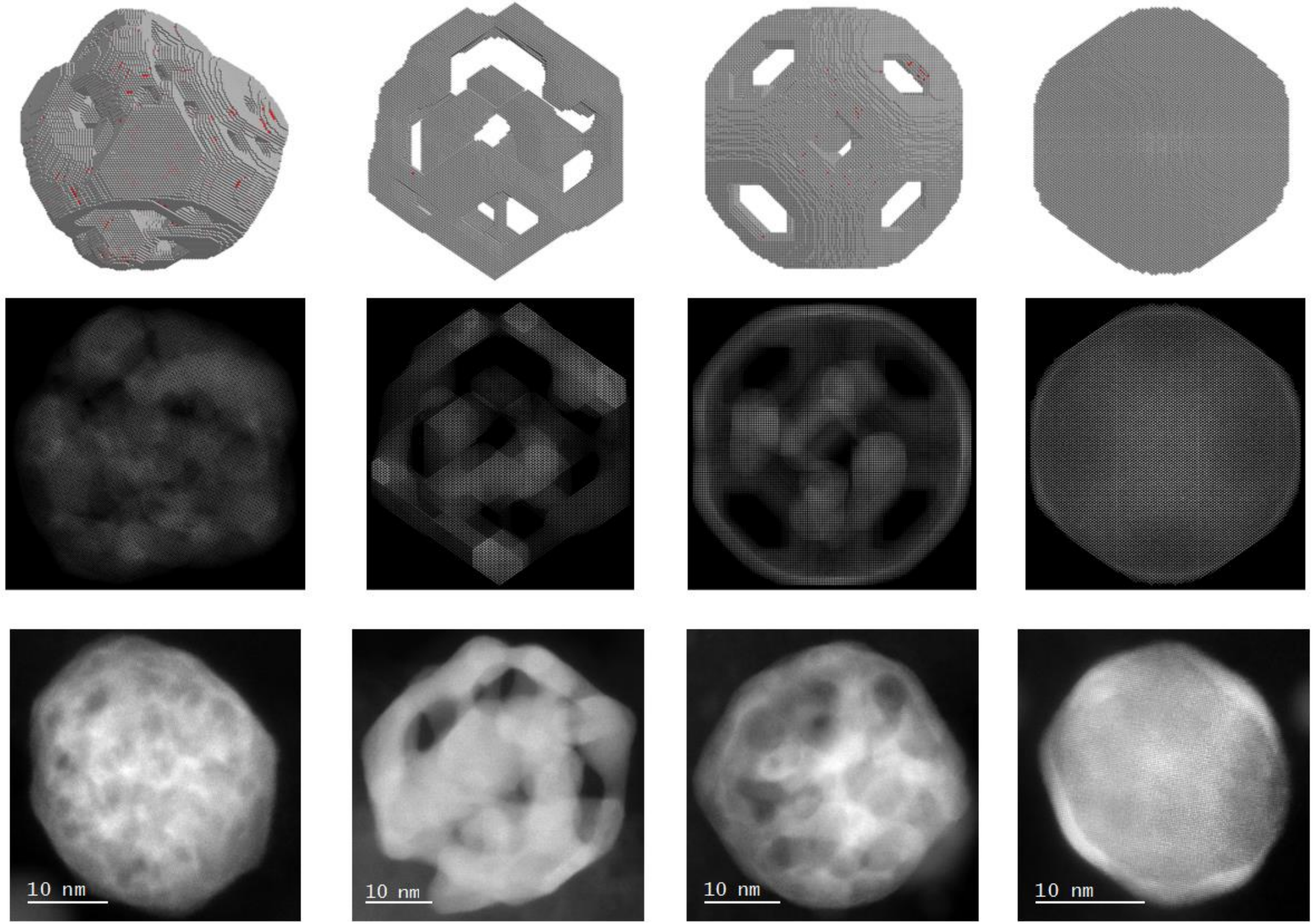
$PtCu_3Au$ dealloying





4 monolayers of Pt

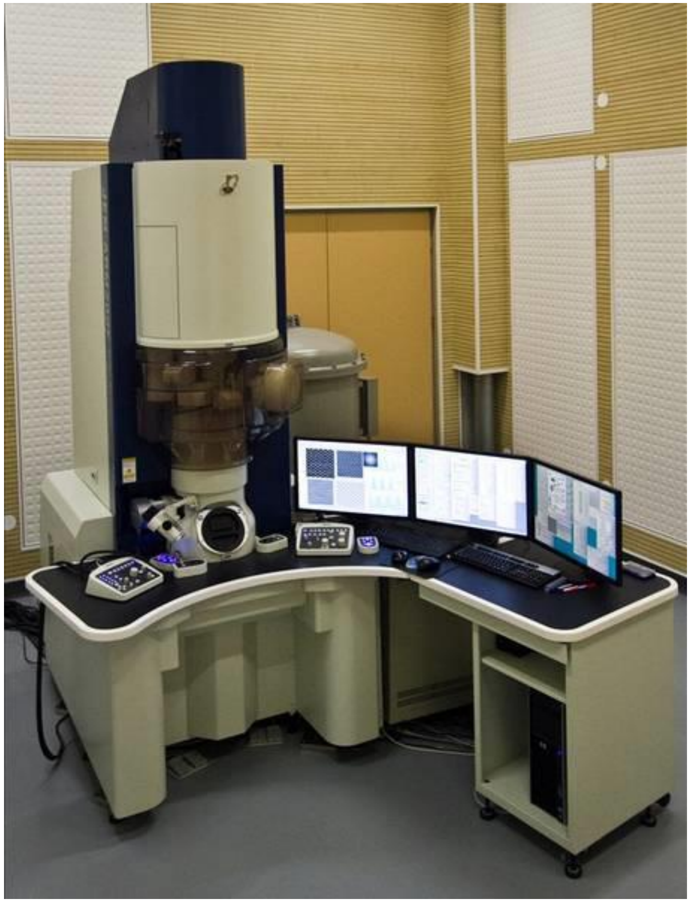
Gatalo, J. Electrochem. Sci. Eng., 2018, 8 (1) pp. 87-100



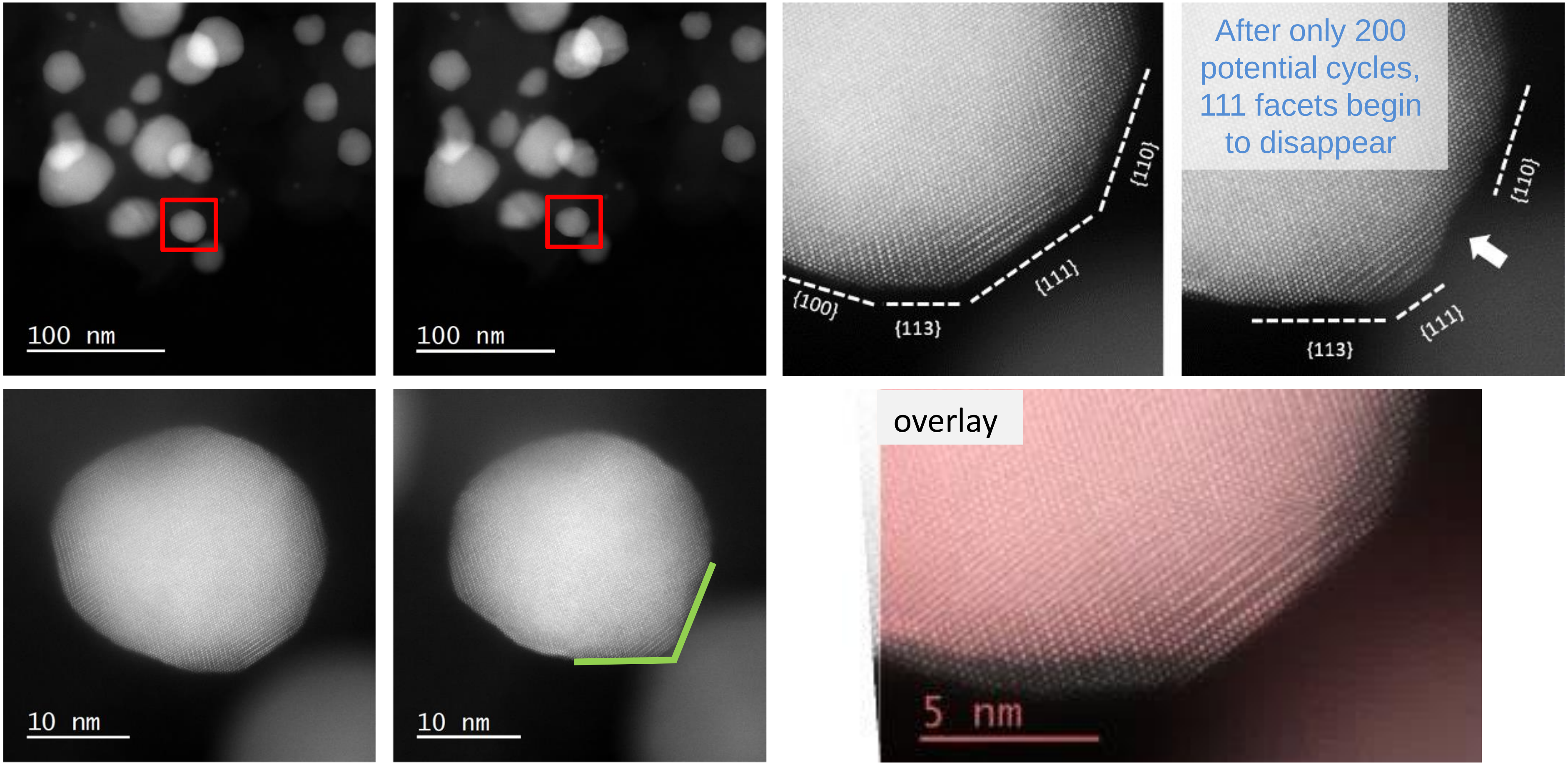
Zepeda, ChemCatChem, 2017

What about atomic resolution?

- AR STEM - a top-of-the-line atomic resolution transmission electron microscope at NIC

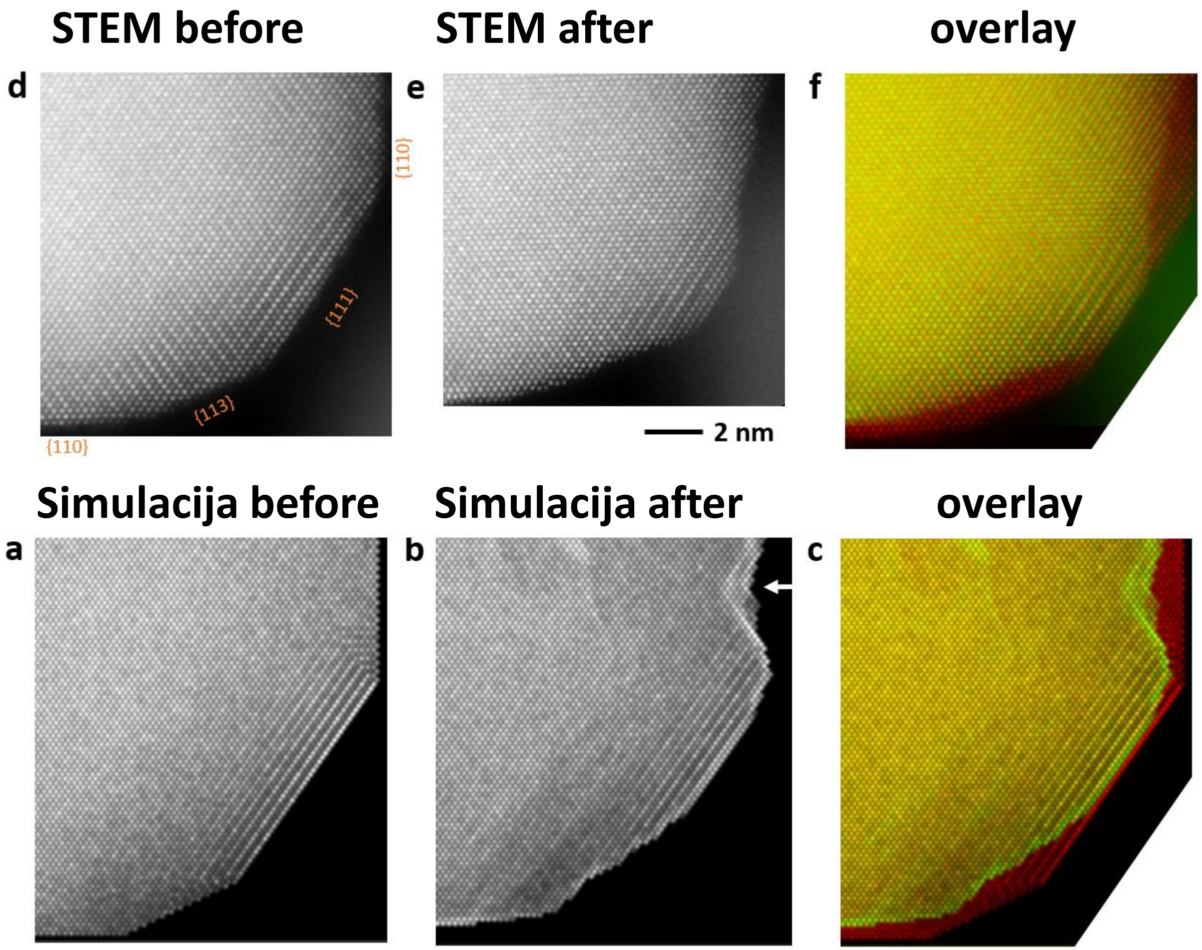


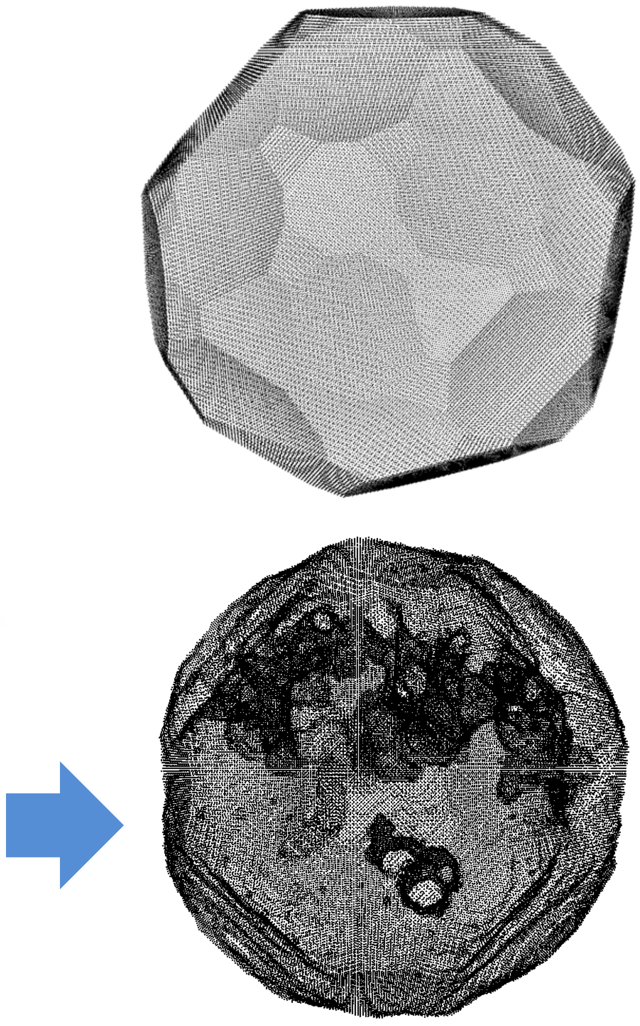
What about atomic resolution?



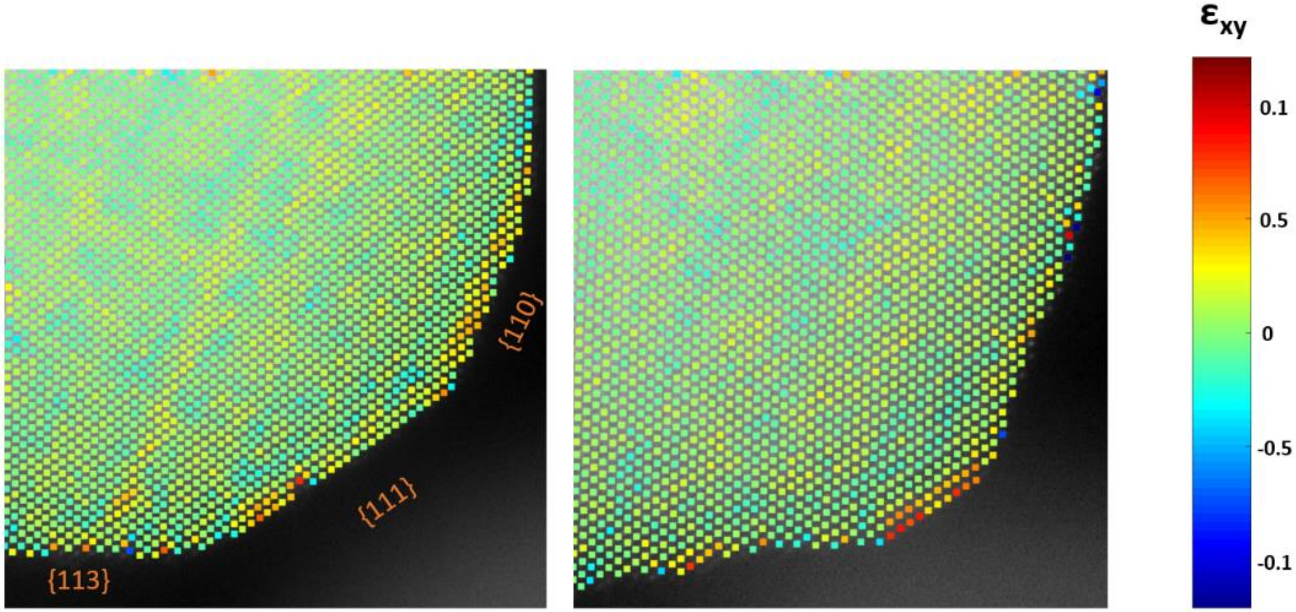
IL-TEM 0,1 M $HClO_4$
200 cyc 0.05 – 1.2 V vs. RHE, 300 mV/s,
Ar

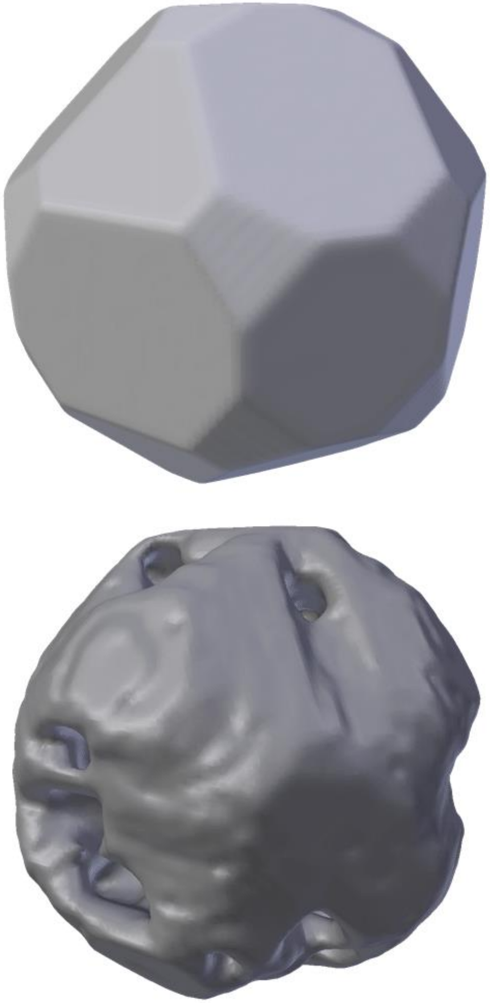
One of our approaches - as a game



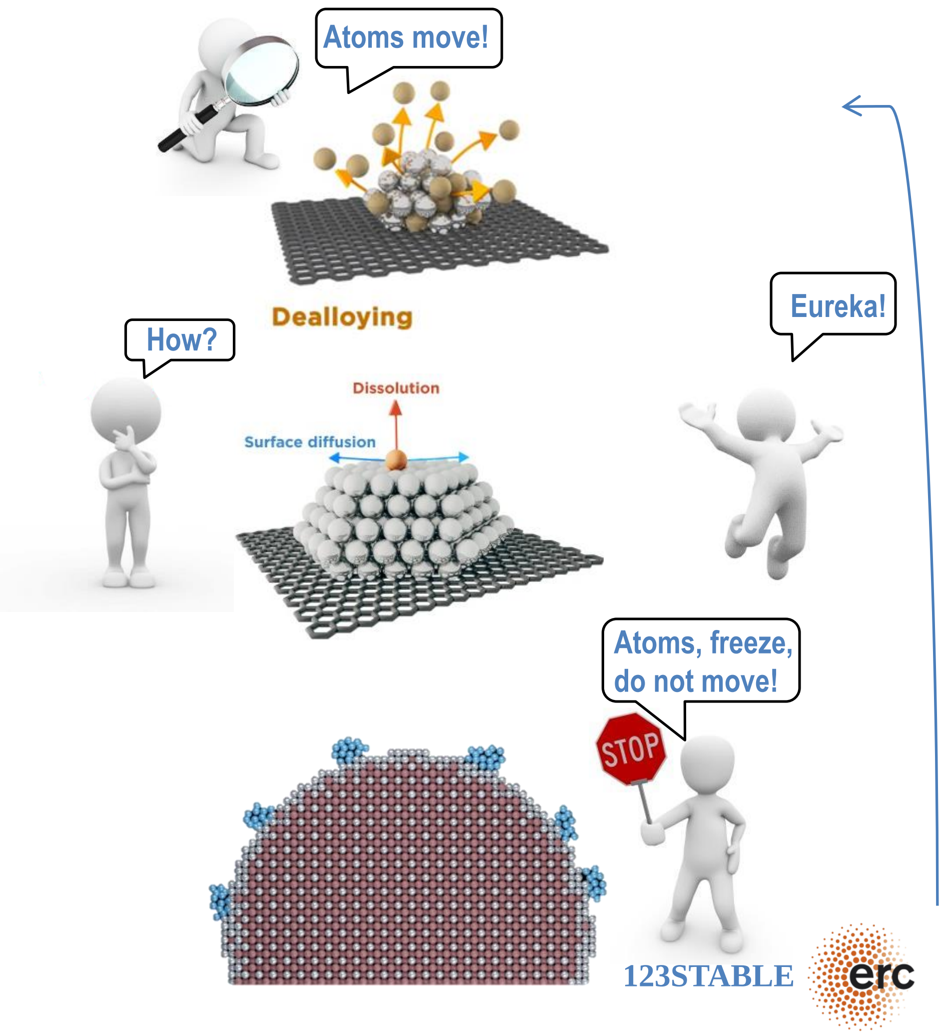


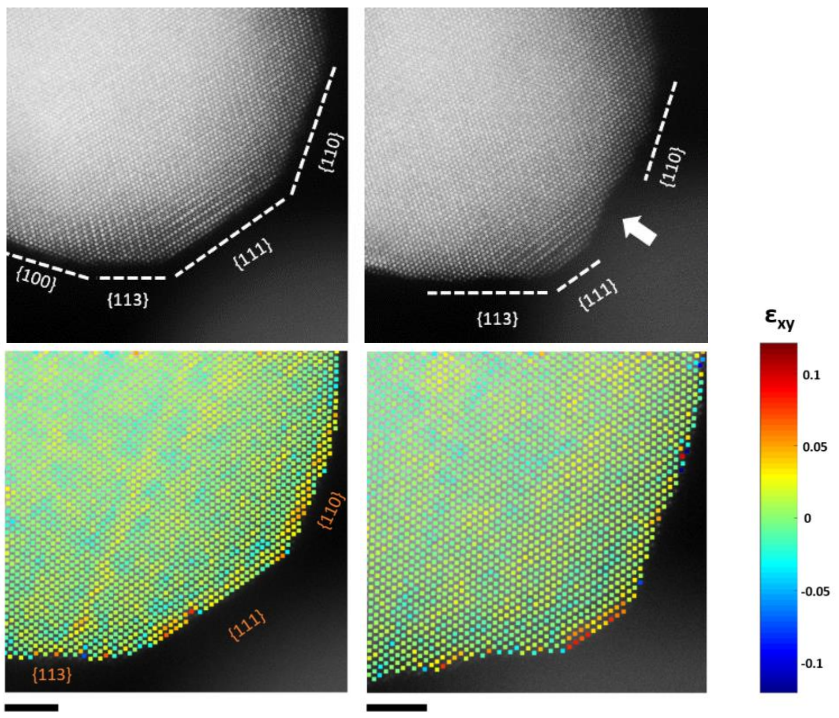
One of our approaches - as a game





Our feedback approach: ERC





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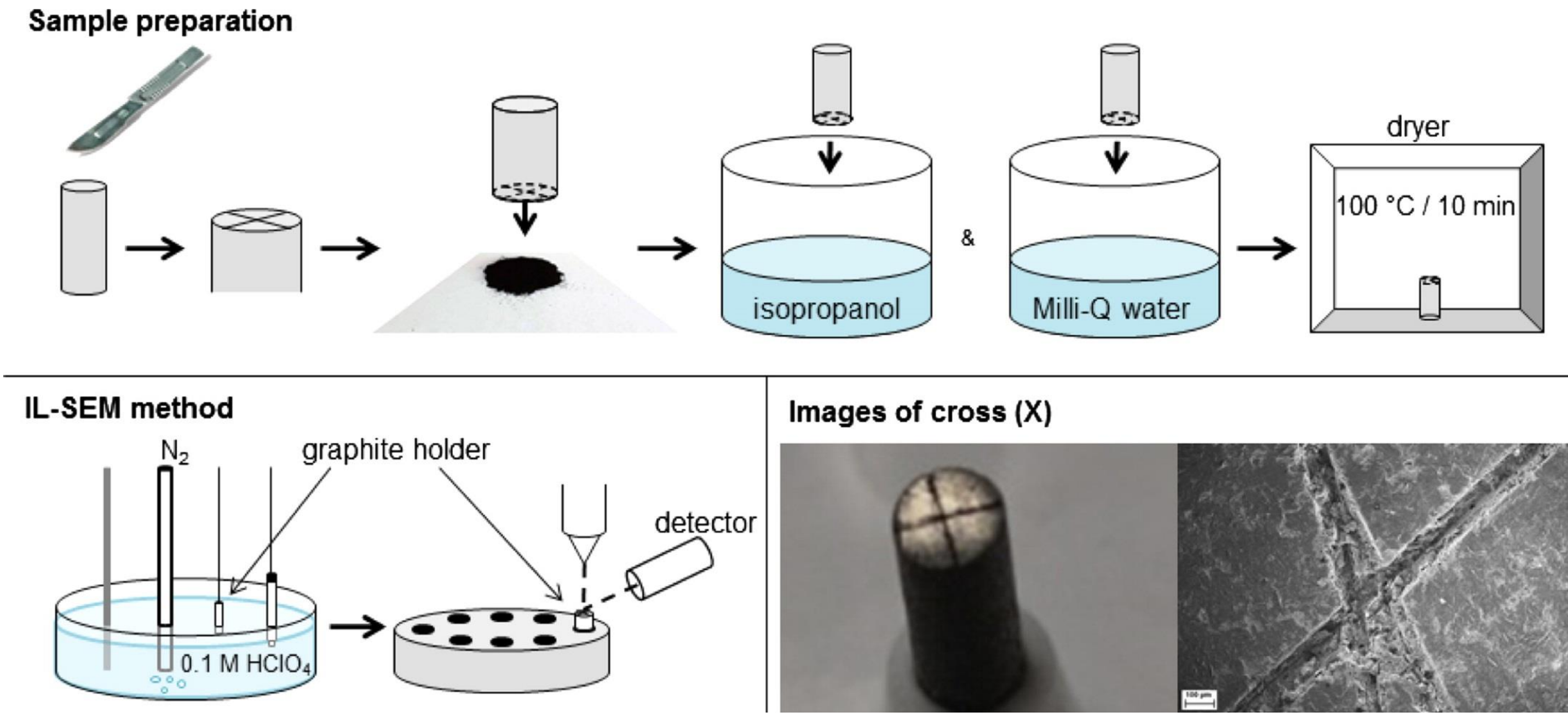
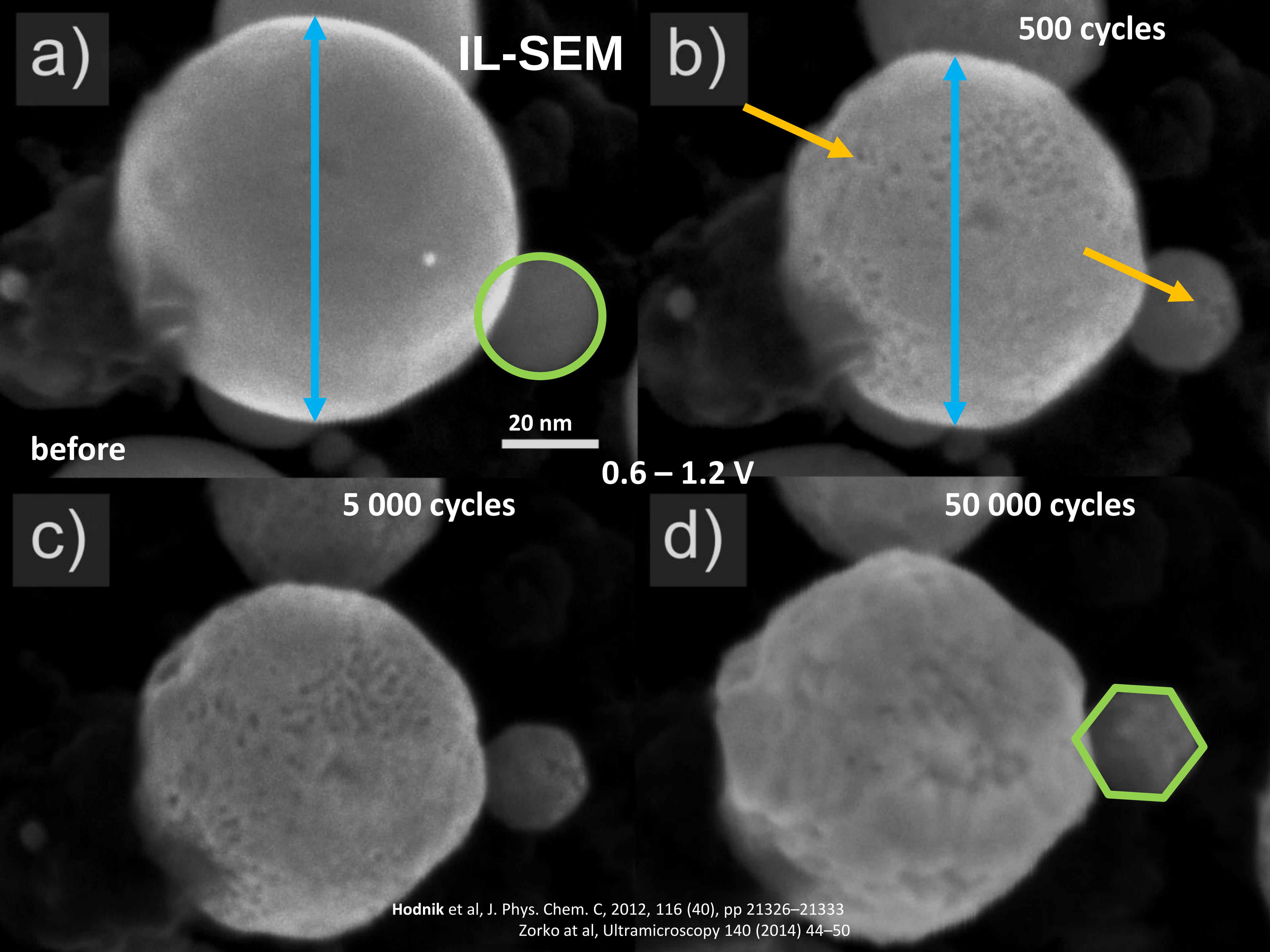
Identical location electron microscopy

Scanning electron microscopy

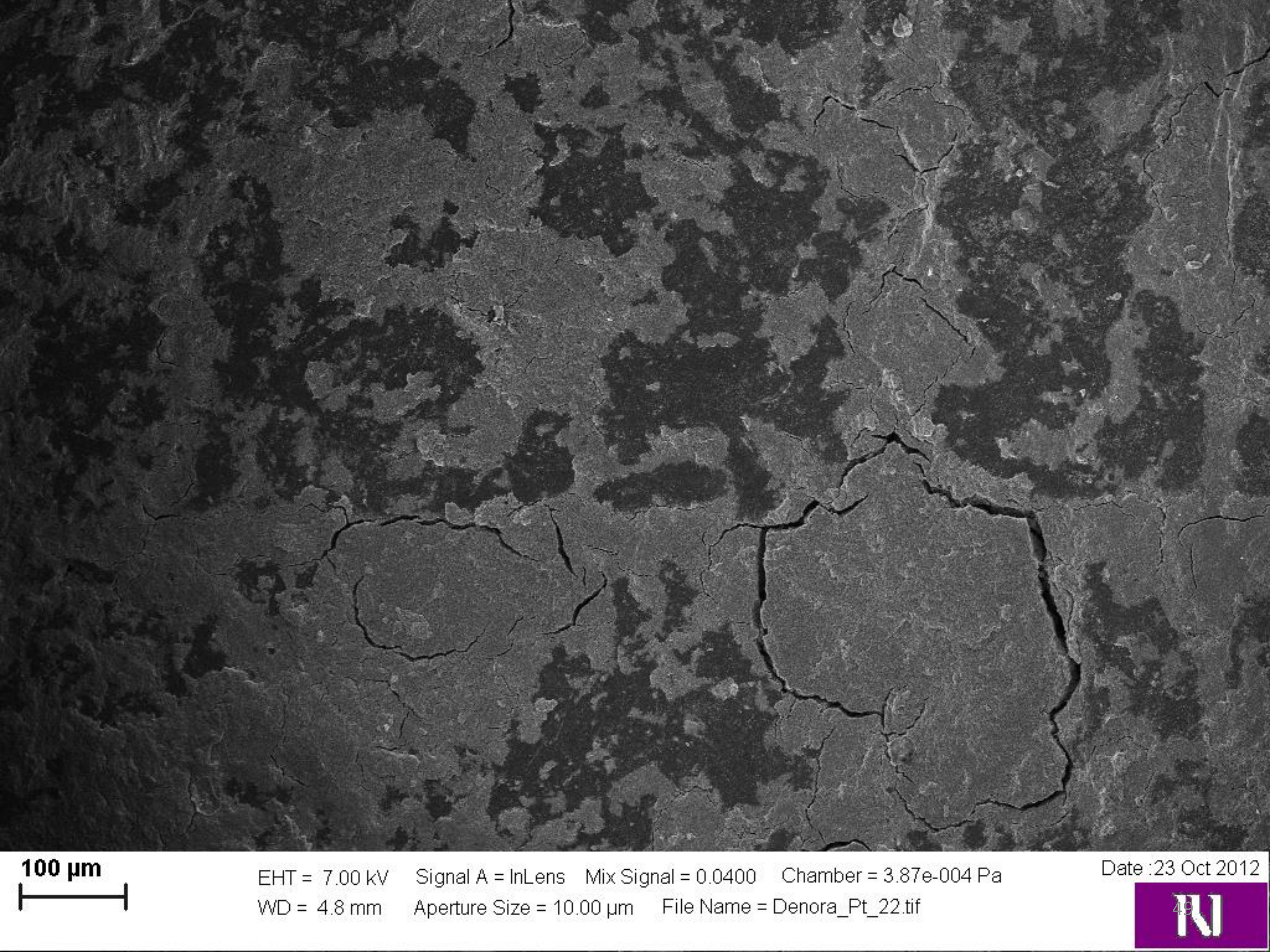


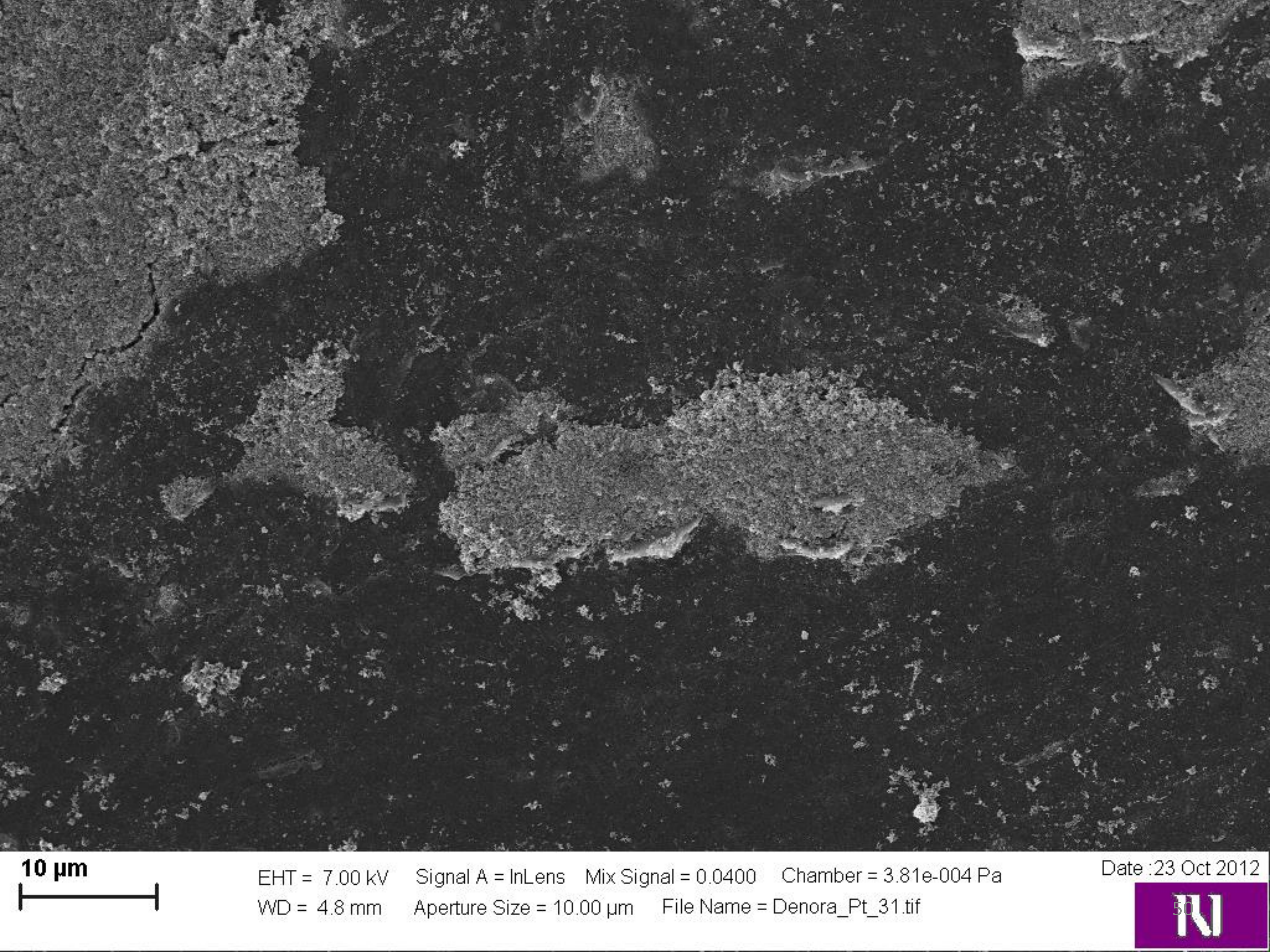
Hodnik, *J. Phys. Chem. C*, **2012,** 116, 21326–21333

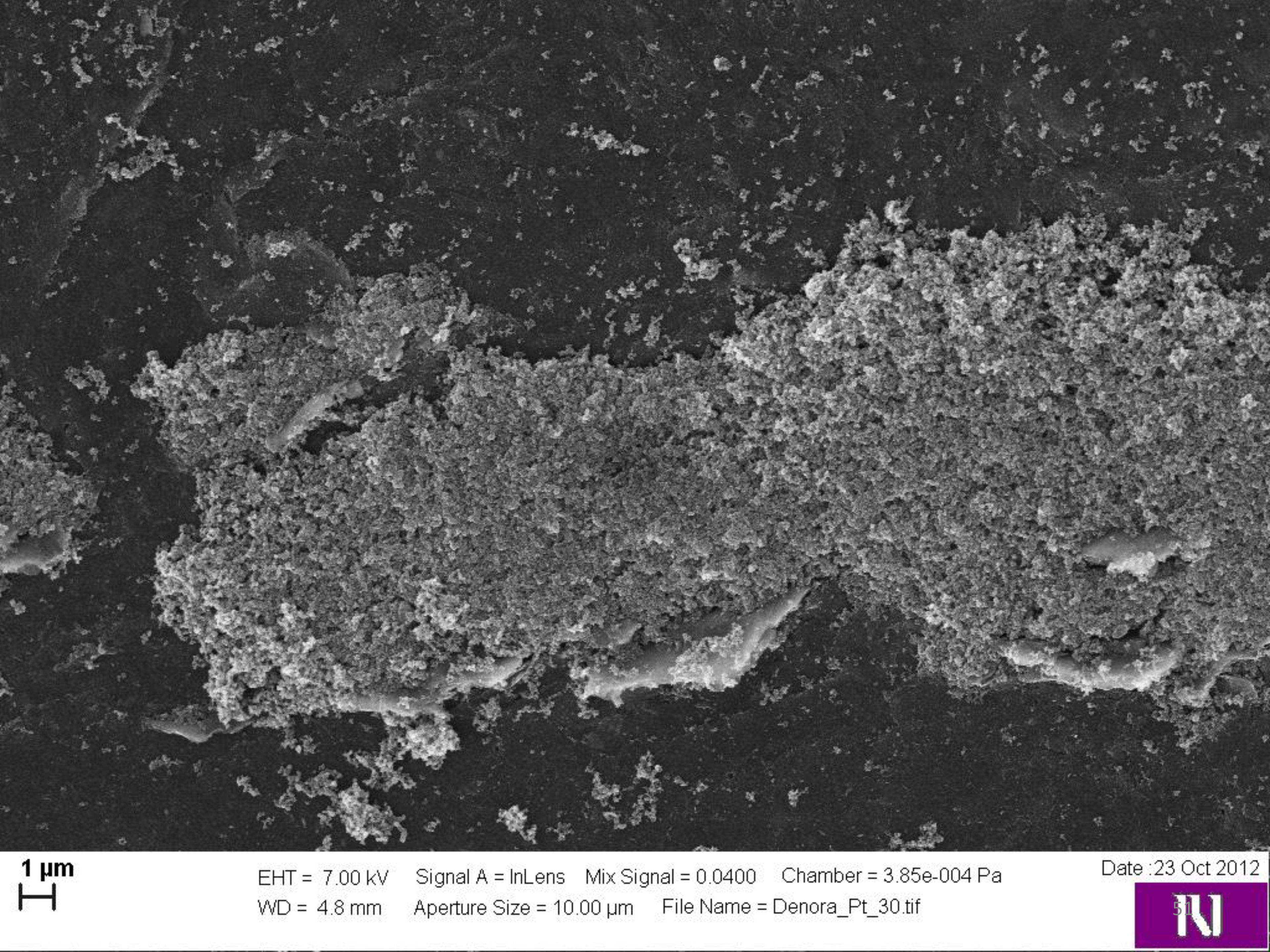
Zorko, *Ultramicroscopy*, **2014,** 140, 44–50

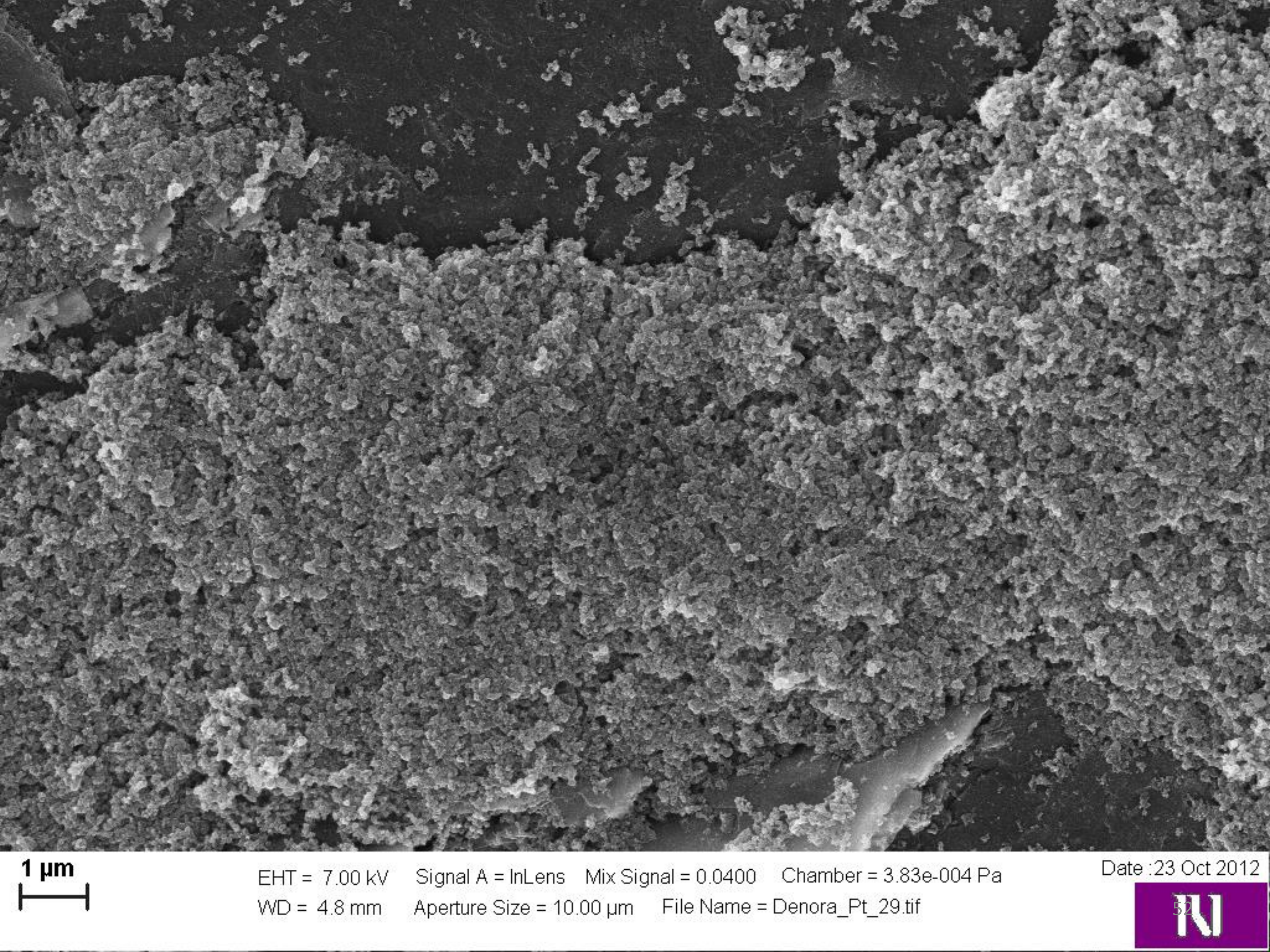


a)
IL-SEM
b)
500 cycles
20 nm
before
0.6 – 1.2 V
c)
5 000 cycles
d)
50 000 cycles
Hodnik et al, J. Phys. Chem. C, 2012, 116 (40), pp 21326–21333
Zorko at al, Ultramicroscopy 140 (2014) 44–50


100 µm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0400
Chamber = 3.87e-004 Pa
Date :23 Oct 2012
WD = 4.8 mm
Aperture Size = 10.00 µm
File Name = Denora_Pt_22.tif


10 µm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0400
Chamber = 3.81e-004 Pa
Date :23 Oct 2012
WD = 4.8 mm
Aperture Size = 10.00 µm
File Name = Denora_Pt_31.tif


1 µm
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_30.tif
Date :23 Oct 2012


1 µm
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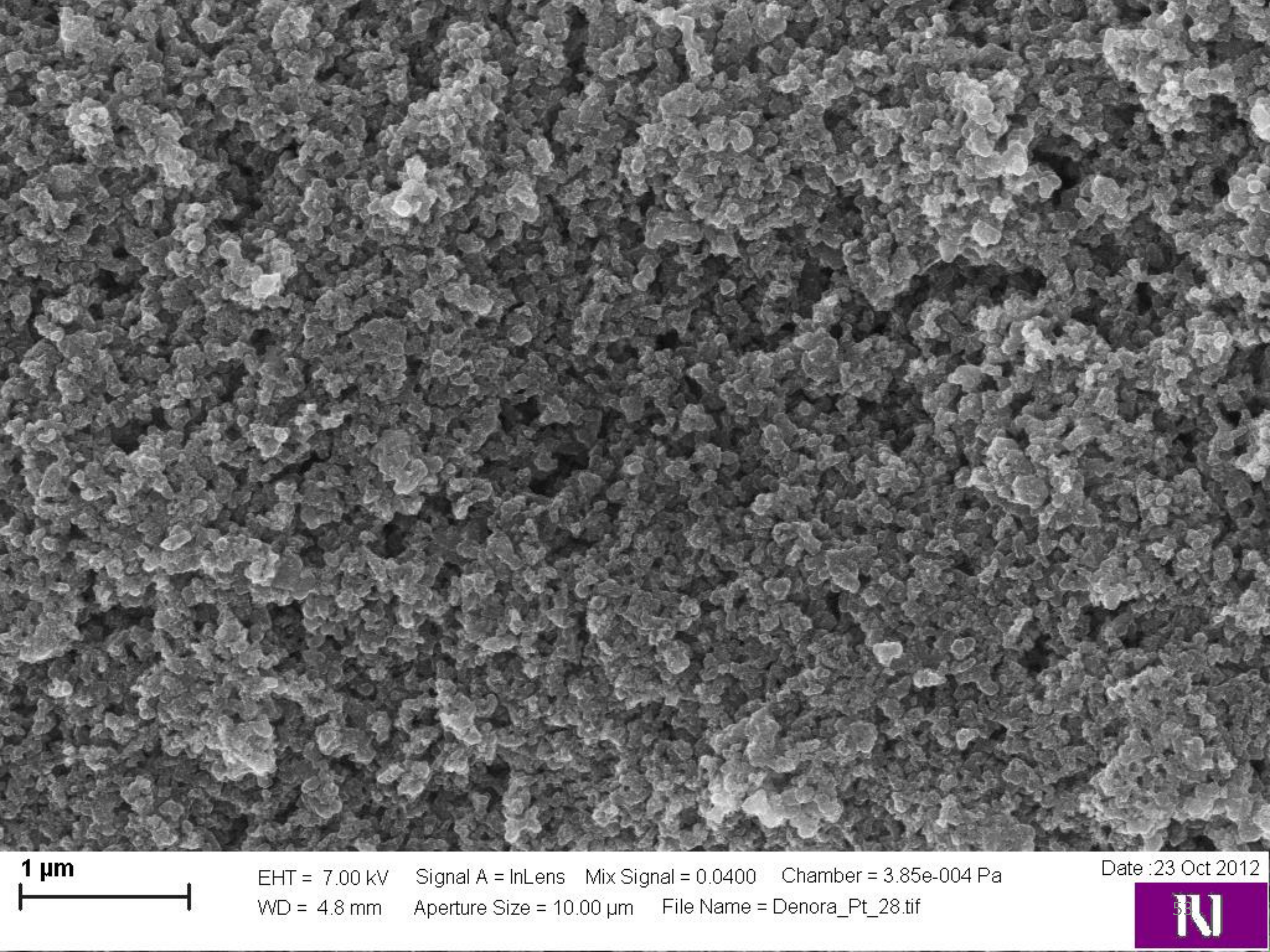
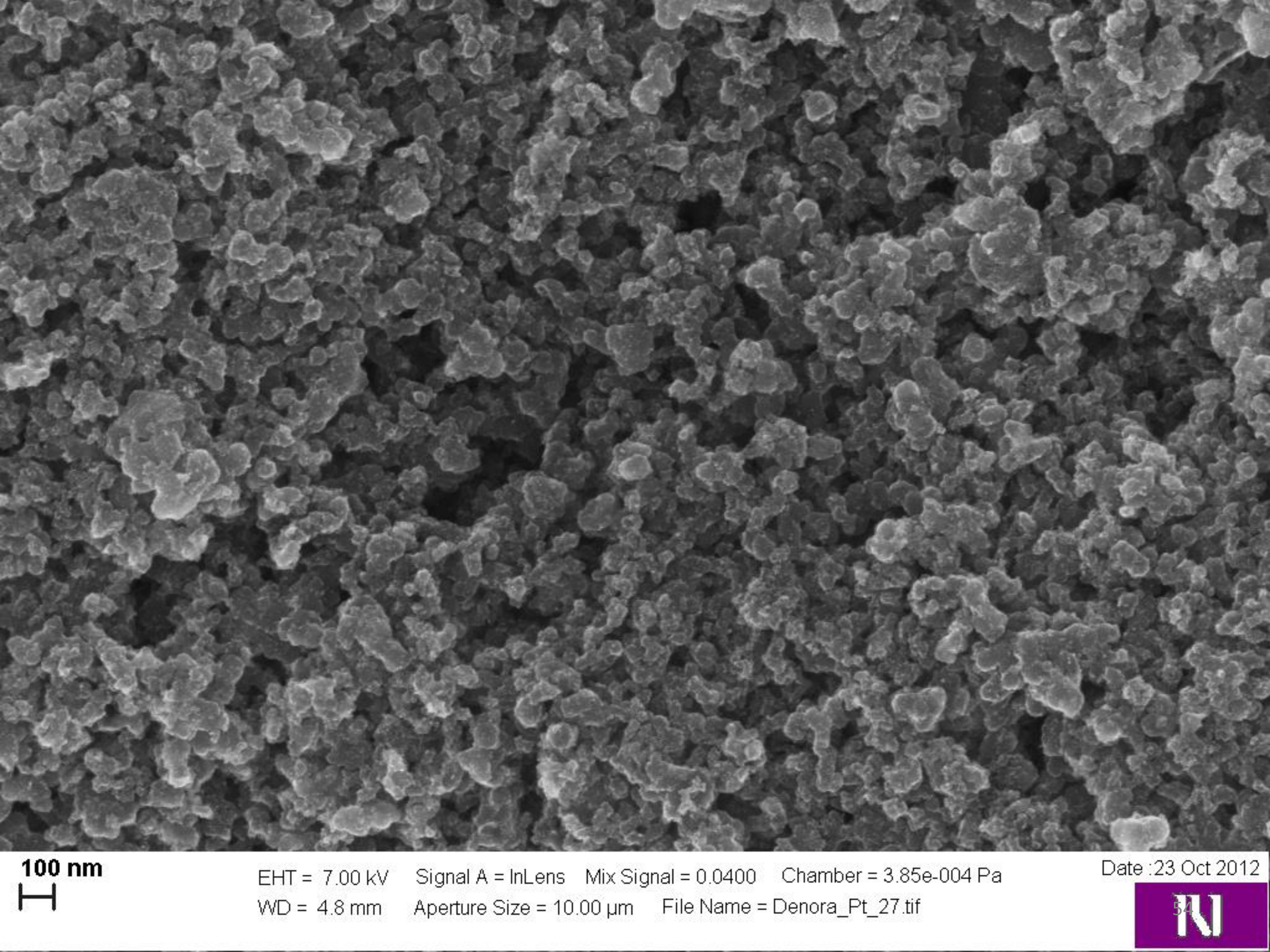
File Name = Denora_Pt_29.tif
Date :23 Oct 2012


1 µm
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_28.tif
Date :23 Oct 2012


100 nm
EHT = 7.00 kV
Signal A = InLens
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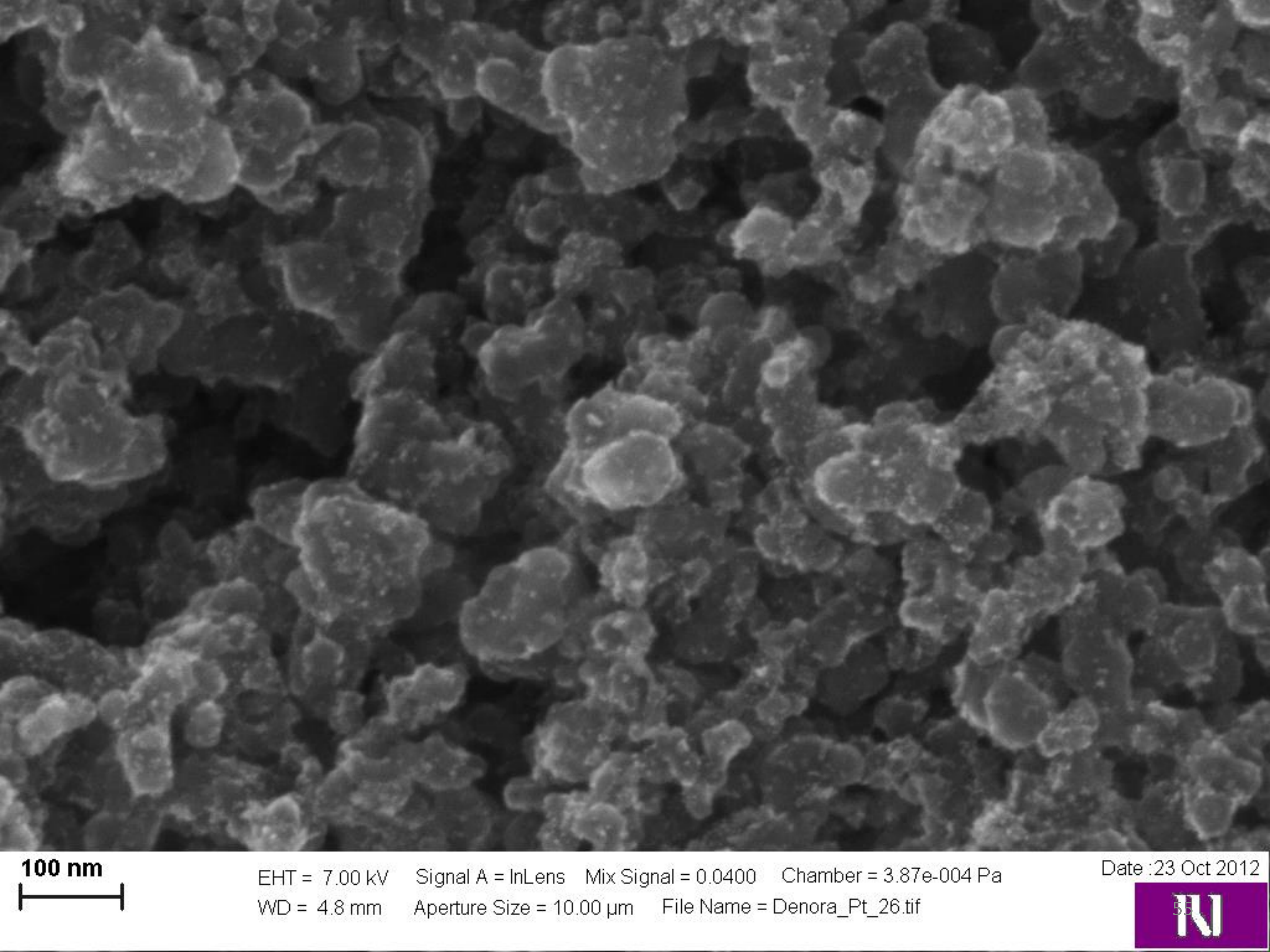
Date :23 Oct 2012
WD = 4.8 mm
Aperture Size = 10.00 µm
File Name = Denora_Pt_27.tif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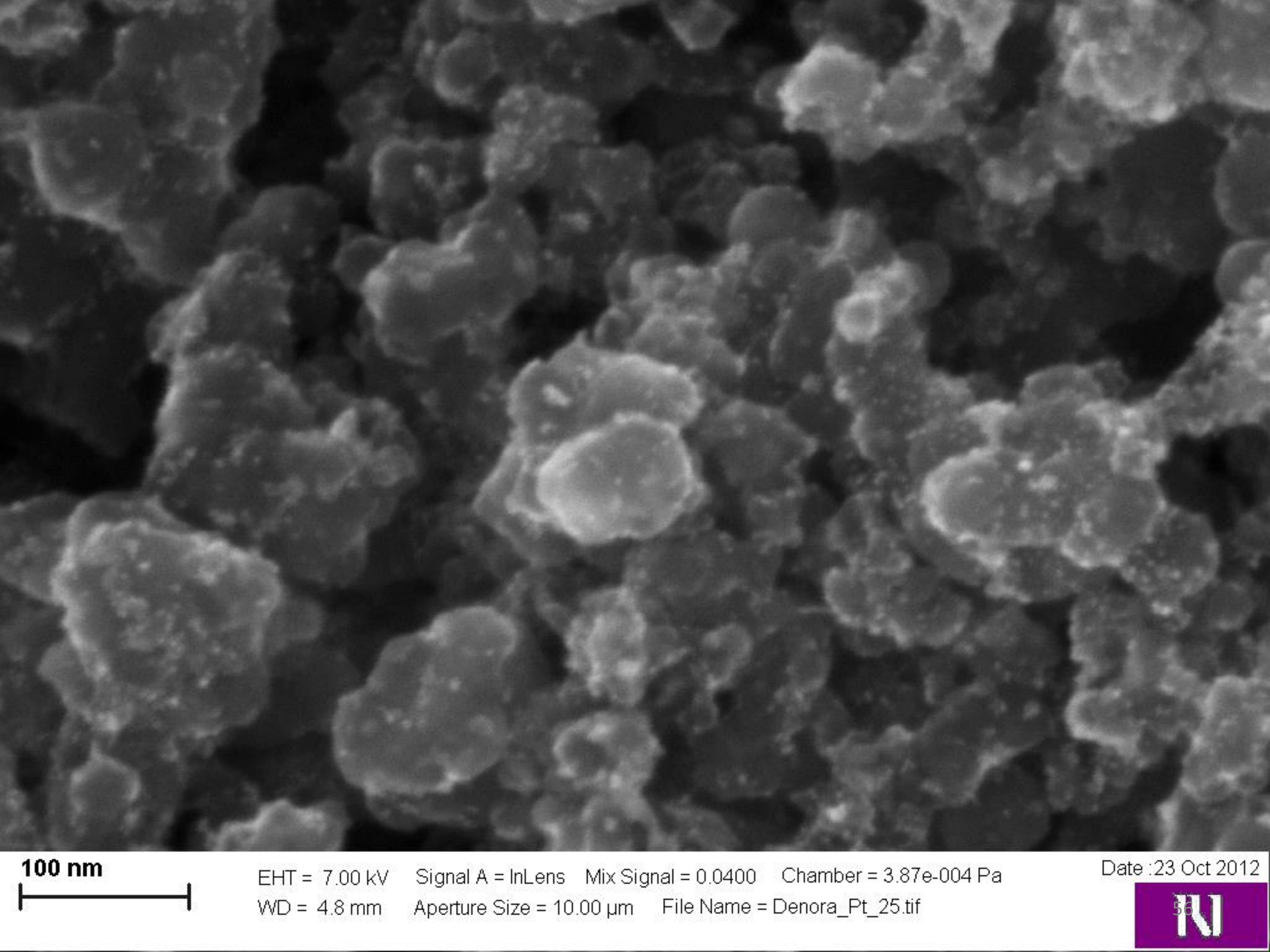
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EHT = 7.00 kV
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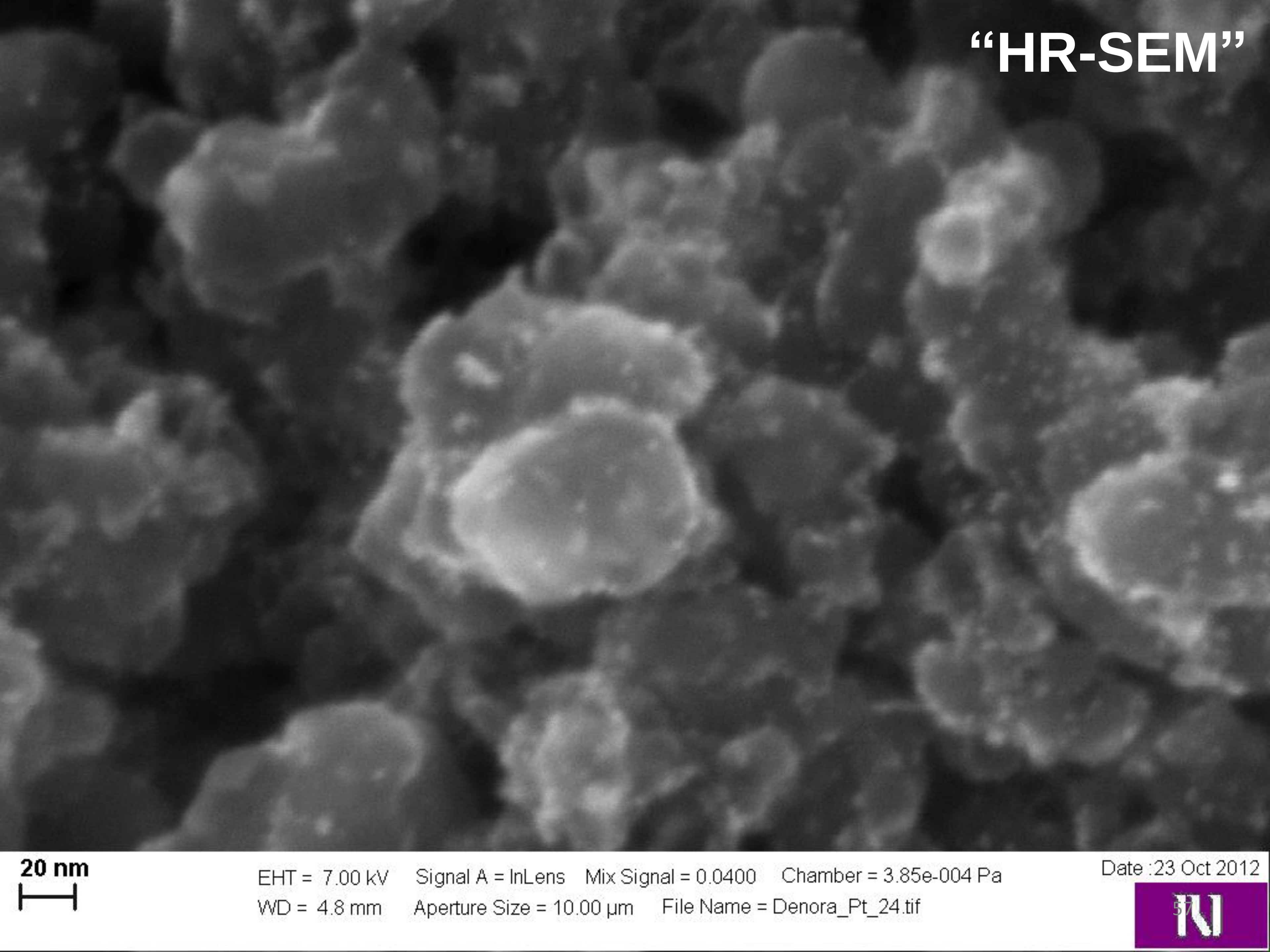
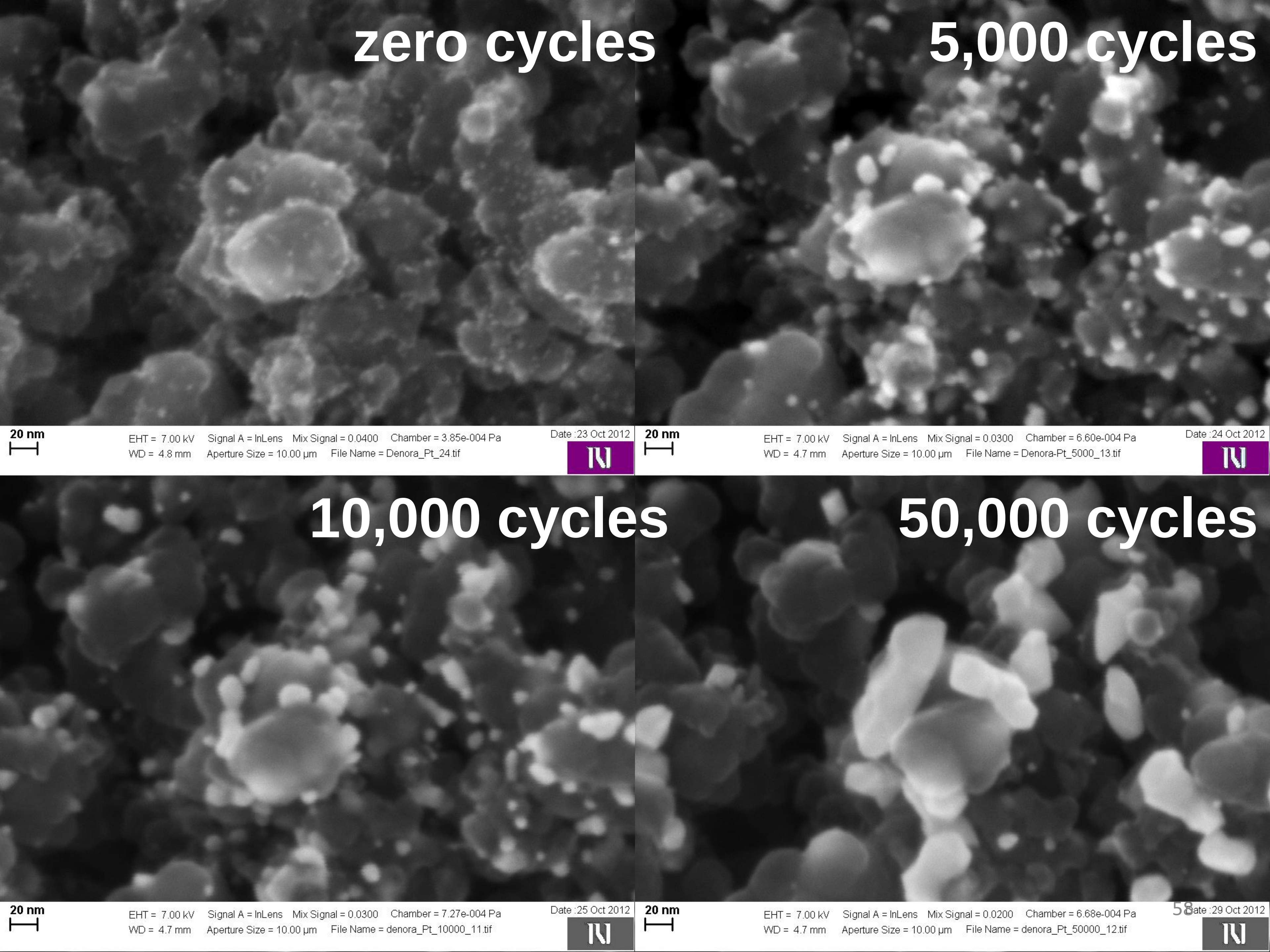
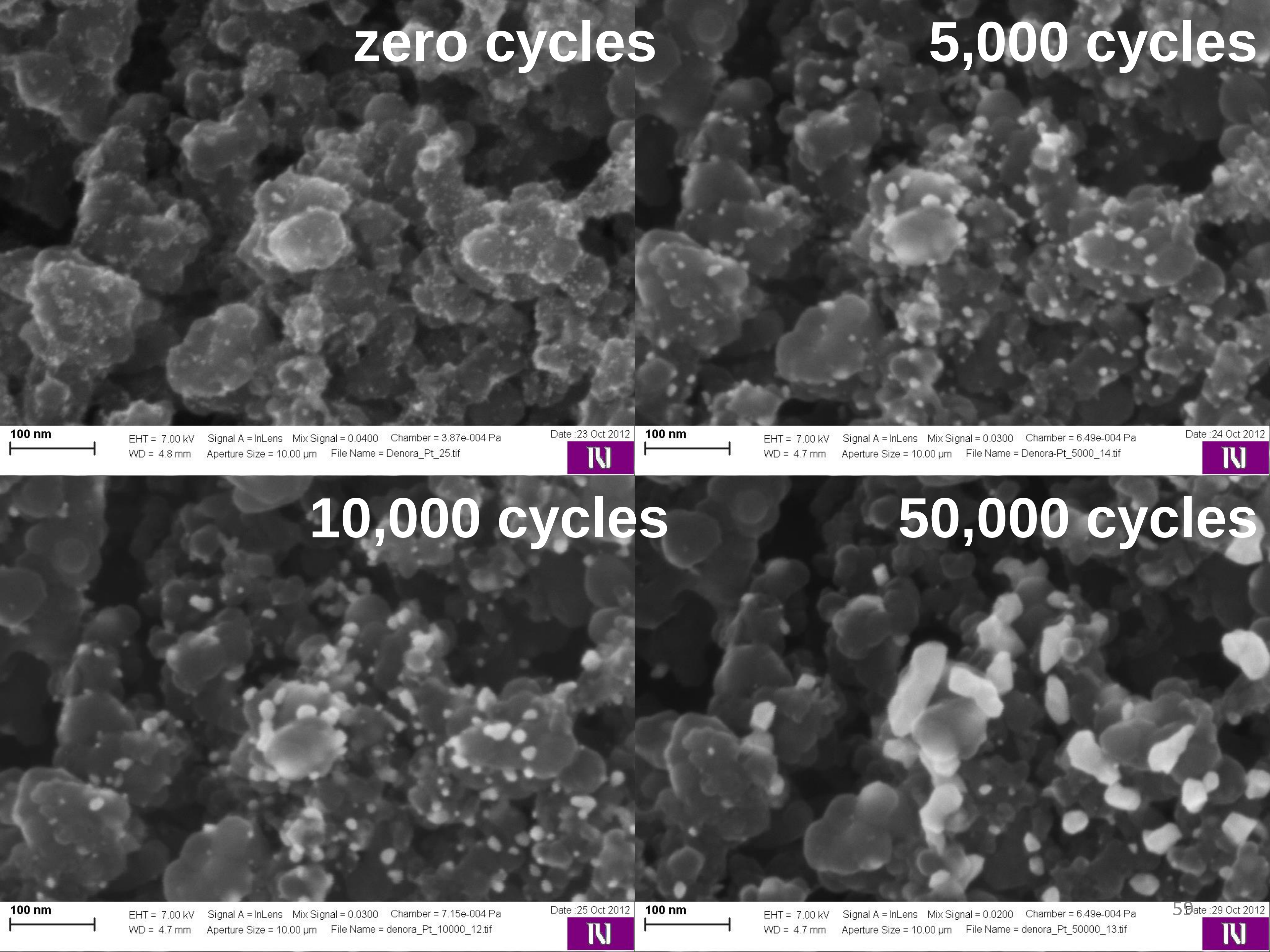
Mix Signal = 0.0400
Chamber = 3.87e-004 Pa
Date :23 Oct 2012
WD = 4.8 mm
Aperture Size = 10.00 µm
File Name = Denora_Pt_25.tif

“HR-SEM”


20 nm
EHT = 7.00 kV
WD = 4.8 mm
Signal A = InLens
Aperture Size = 10.00 µm
Mix Signal = 0.0400
File Name = Denora_Pt_24.tif
Chamber = 3.85e-004 Pa
Date :23 Oct 2012



zero cycles
20 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_24.tif
Date :23 Oct 2012
5,000 cycles
20 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0300 Chamber = 6.60e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = Denora-Pt_5000_13.tif
Date :24 Oct 2012
10,000 cycles
20 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0300 Chamber = 7.27e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_10000_11.tif
Date :25 Oct 2012
50,000 cycles
20 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0200 Chamber = 6.68e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_50000_12.tif
Date :29 Oct 2012


zero cycles
100 nm
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WD = 4.8 mm Aperture Size = 10.00 µm File Name = Denora_Pt_25.tif
Date :23 Oct 2012
5,000 cycles
100 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0300 Chamber = 6.49e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = Denora-Pt_5000_14.tif
Date :24 Oct 2012
10,000 cycles
100 nm
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100 nm
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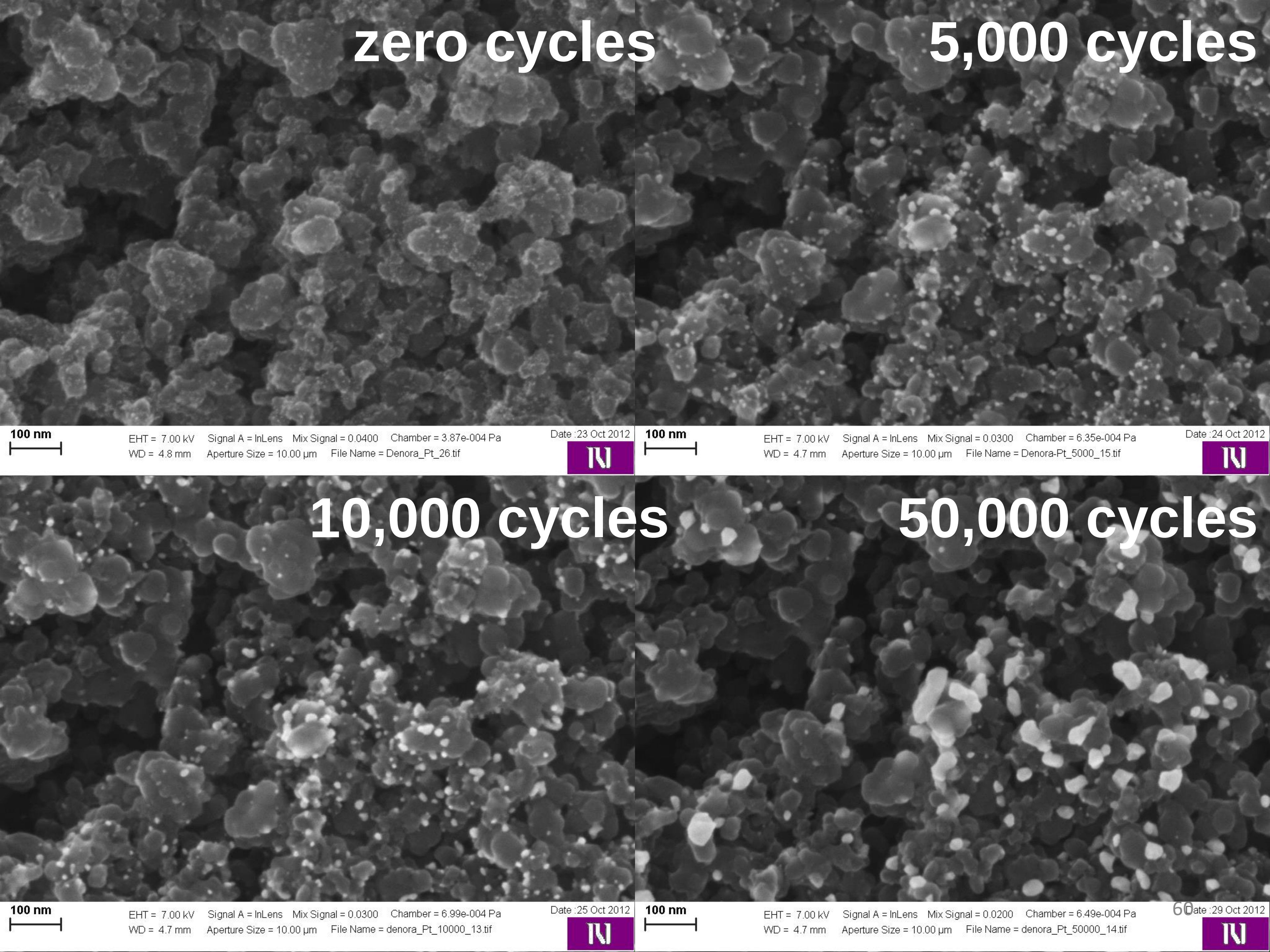
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_50000_13.tif
Date :29 Oct 2012


zero cycles
5,000 cycles
10,000 cycles
50,000 cycles
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0400
Chamber = 3.87e-004 Pa
Date :23 Oct 2012
WD = 4.8 mm
Aperture Size = 10.00 µm
File Name = Denora_Pt_26.tif
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0300
Chamber = 6.35e-004 Pa
Date :24 Oct 2012
WD = 4.7 mm
Aperture Size = 10.00 µm
File Name = Denora-Pt_5000_15.tif
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0300
Chamber = 6.99e-004 Pa
Date :25 Oct 2012
WD = 4.7 mm
Aperture Size = 10.00 µm
File Name = denora_Pt_10000_13.tif
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0200
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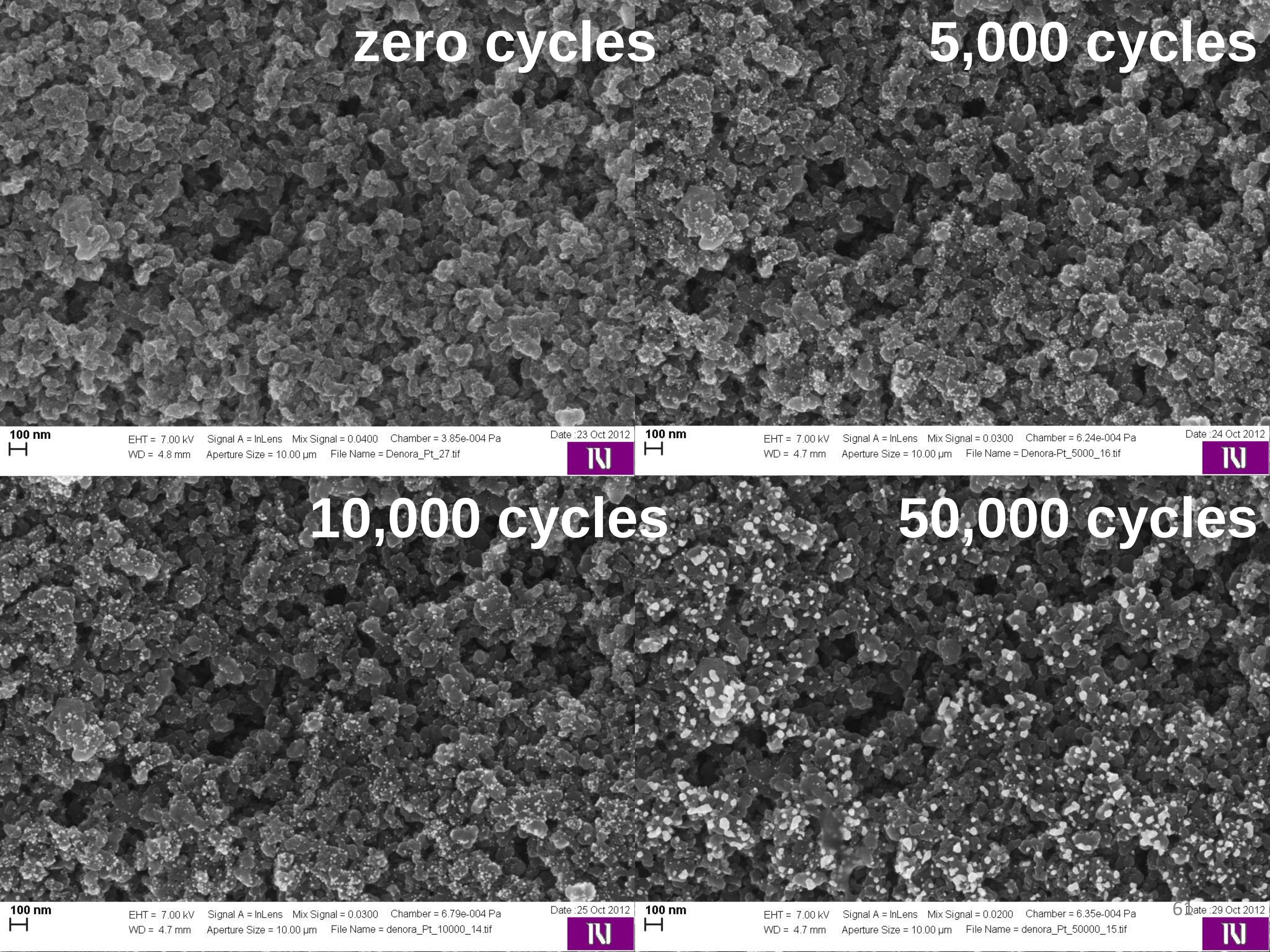
Date :29 Oct 2012
WD = 4.7 mm
Aperture Size = 10.00 µm
File Name = denora_Pt_50000_14.tif


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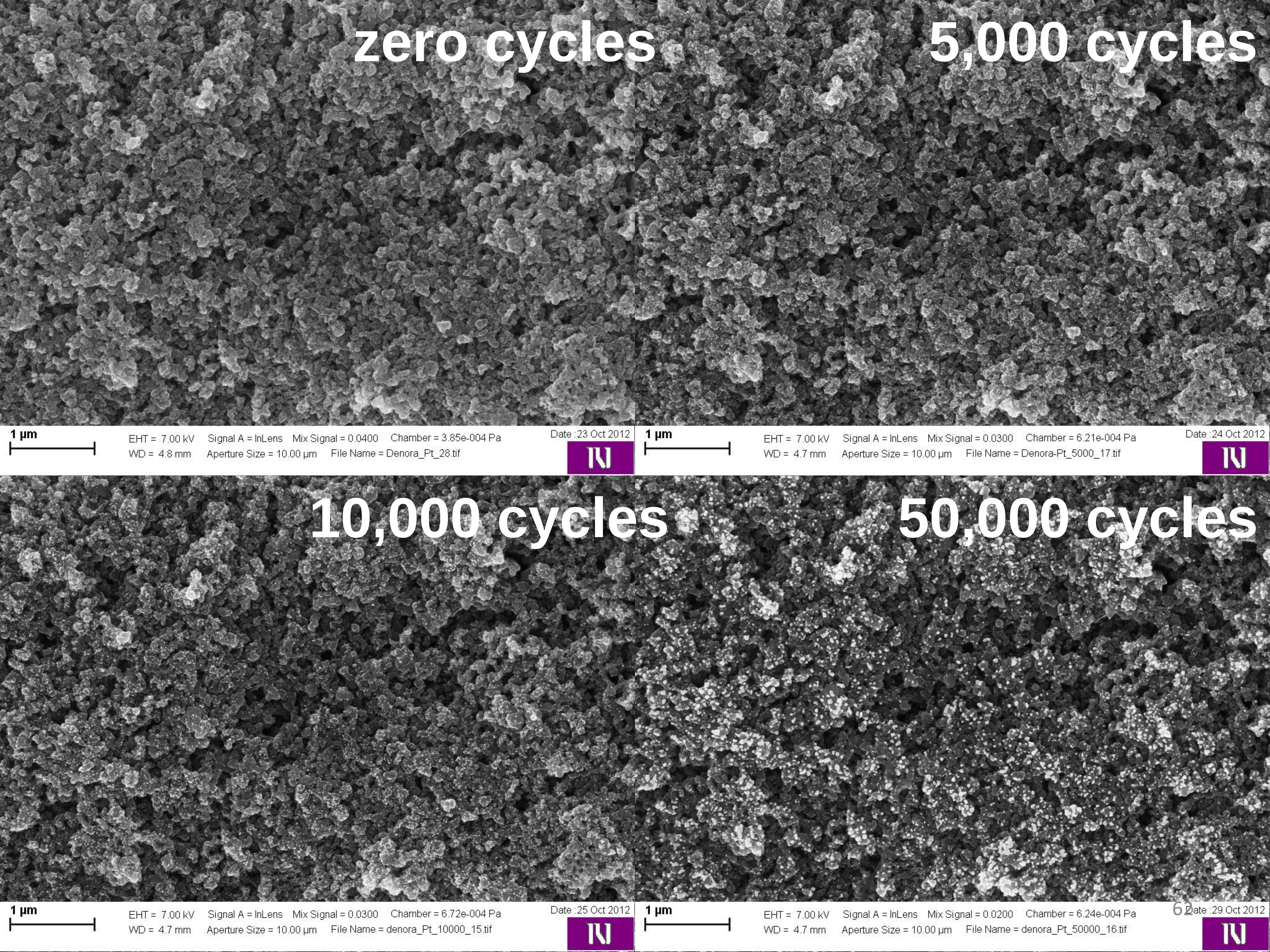
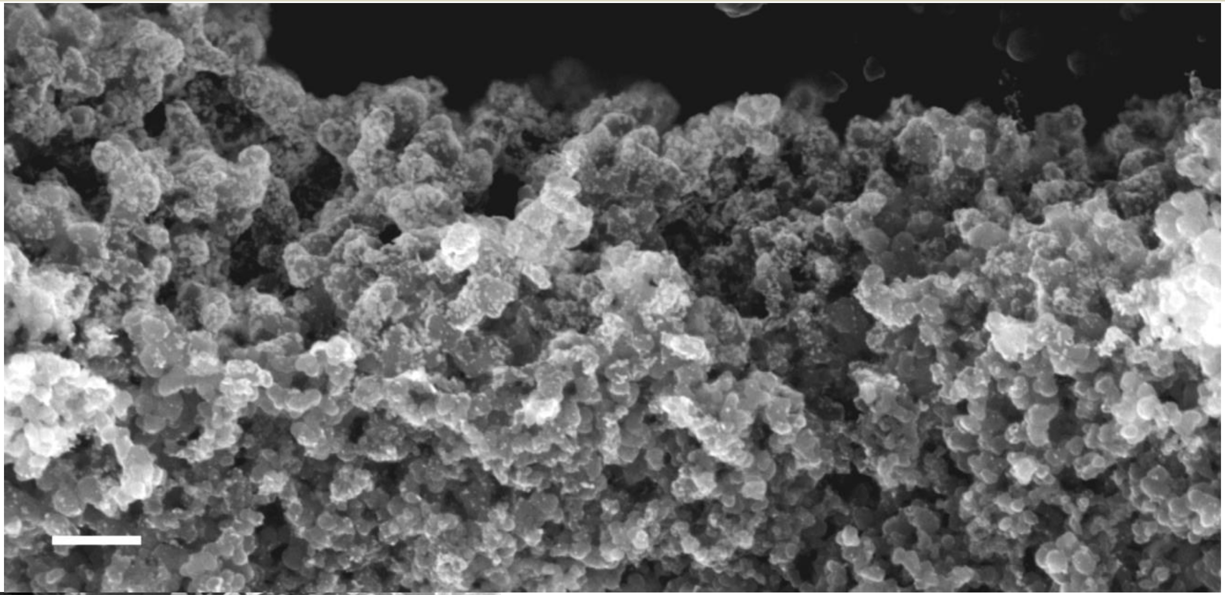
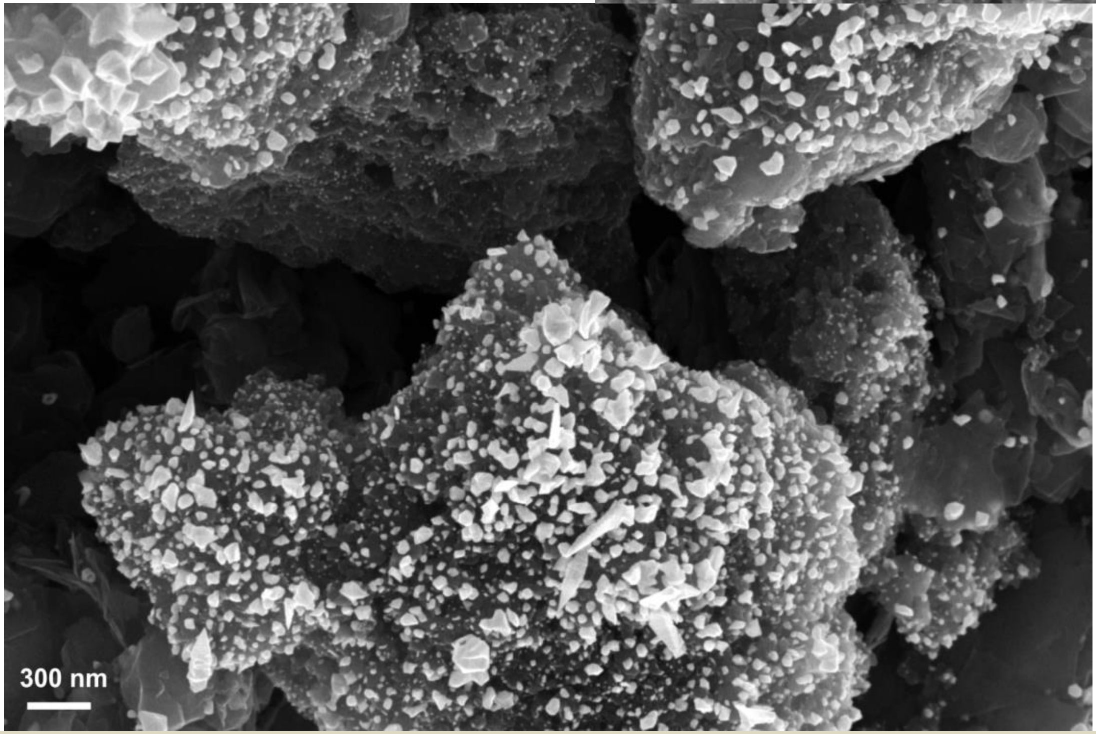
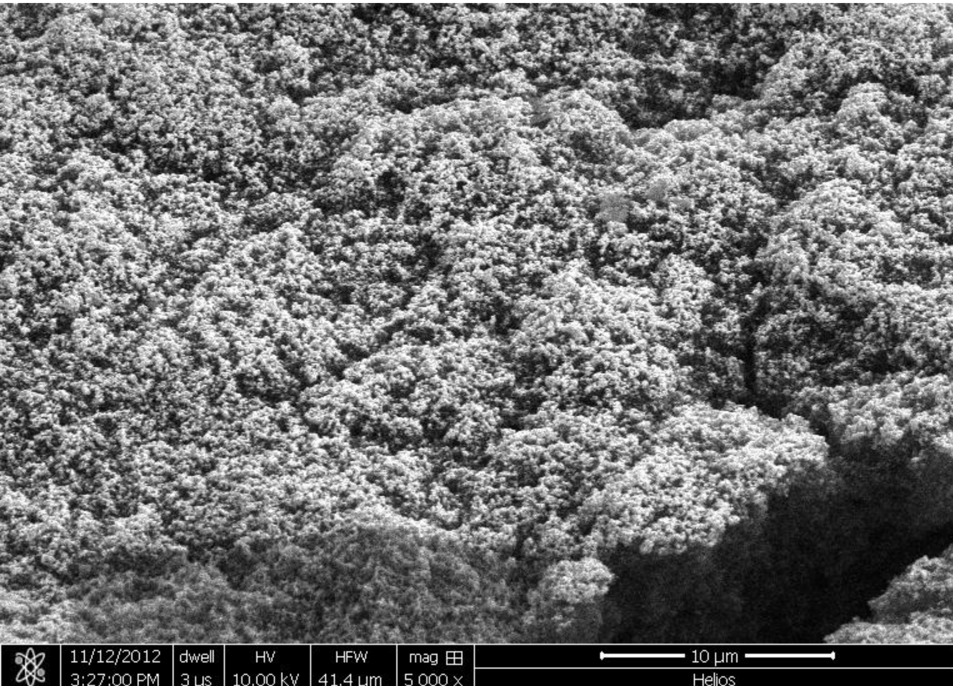
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_10000_14.tif
Date :25 Oct 2012
100 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0200 Chamber = 6.35e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_50000_15.tif
Date :29 Oct 2012

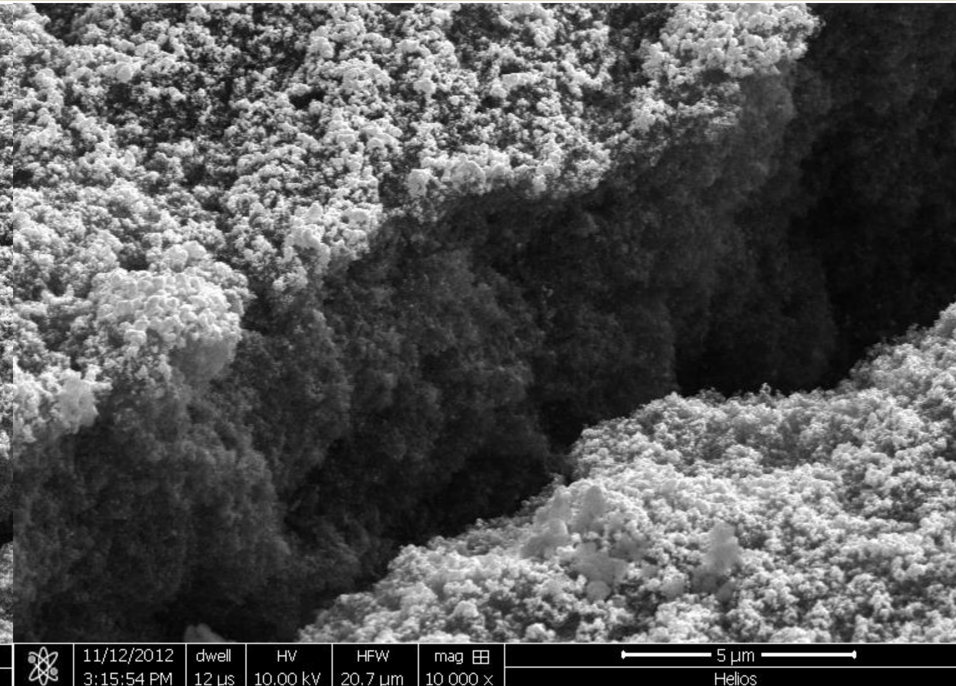

zero cycles
1 µm
EHT = 7.00 kV
WD = 4.8 mm
Signal A = InLens
Aperture Size = 10.00 µm
Mix Signal = 0.0400
File Name = Denora_Pt_28.tif
Chamber = 3.85e-004 Pa
Date :23 Oct 2012
5,000 cycles
1 µm
EHT = 7.00 kV
WD = 4.7 mm
Signal A = InLens
Aperture Size = 10.00 µm
Mix Signal = 0.0300
File Name = Denora-Pt_5000_17.tif
Chamber = 6.21e-004 Pa
Date :24 Oct 2012
10,000 cycles
1 µm
EHT = 7.00 kV
WD = 4.7 mm
Signal A = InLens
Aperture Size = 10.00 µm
Mix Signal = 0.0300
File Name = denora_Pt_10000_15.tif
Chamber = 6.72e-004 Pa
Date :25 Oct 2012
50,000 cycles
1 µm
EHT = 7.00 kV
WD = 4.7 mm
Signal A = InLens
Aperture Size = 10.00 µm
Mix Signal = 0.0200
File Name = denora_Pt_50000_16.tif
Chamber = 6.24e-004 Pa
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
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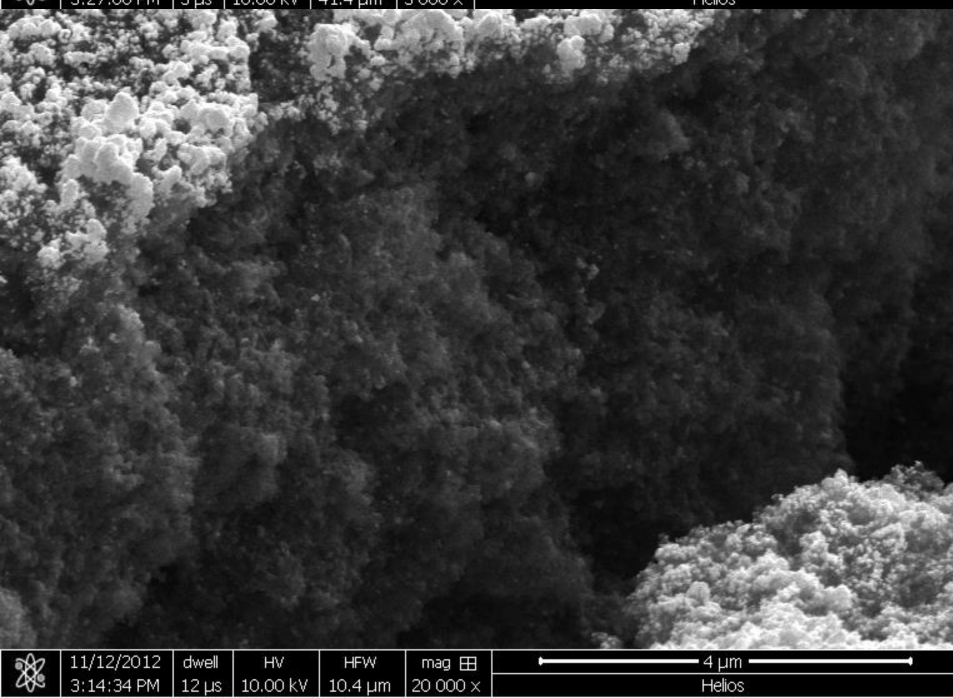
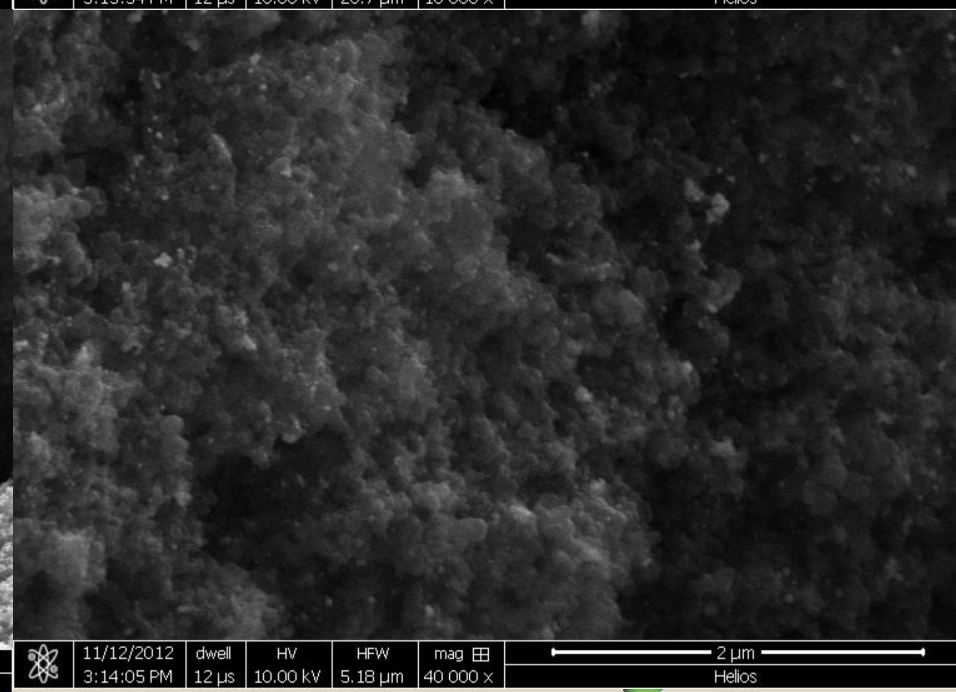
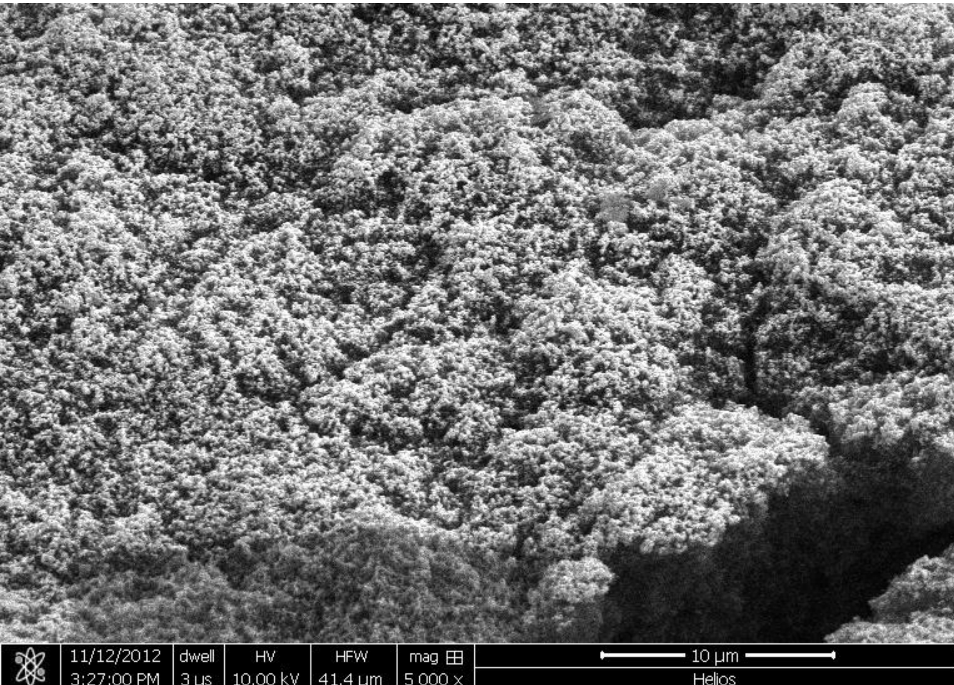
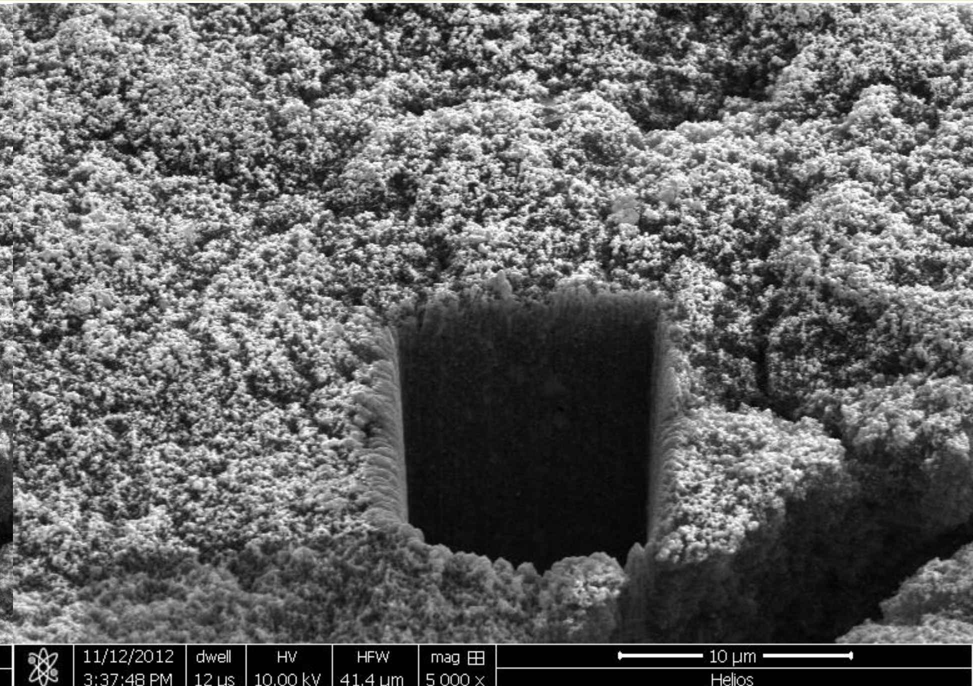
dwell
12 µs
HV
10.00 kV
HFW
20.7 µm
mag ⊞
10 000 x
5 µm
Helios

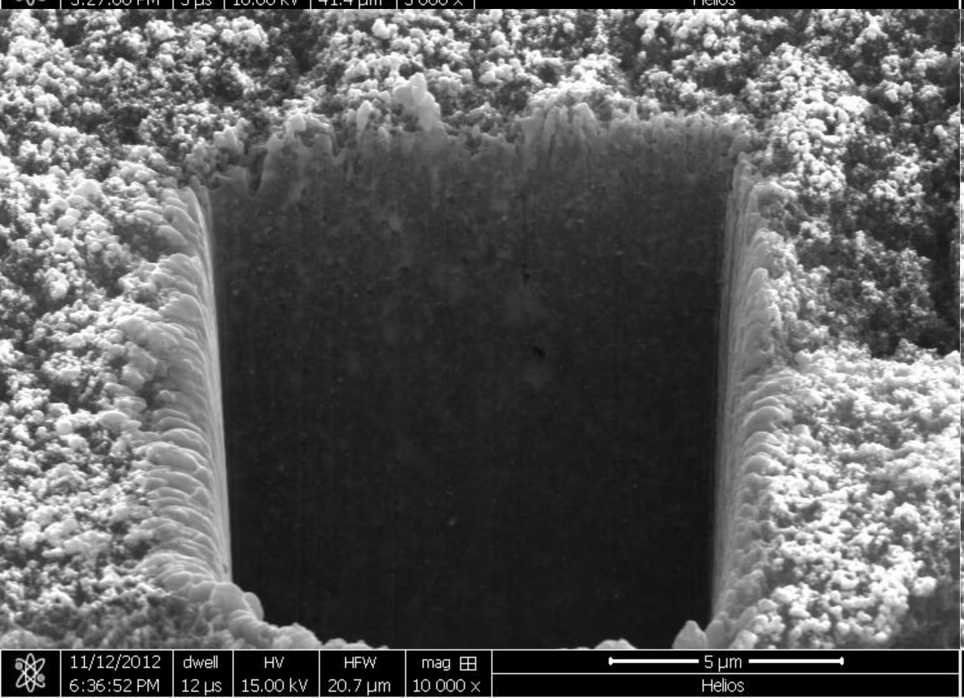

11/12/2012
3:14:34 PM
dwell
12 µs
HV
10.00 kV
HFW
10.4 µm
mag ⊞
20 000 x
4 µm
Helios

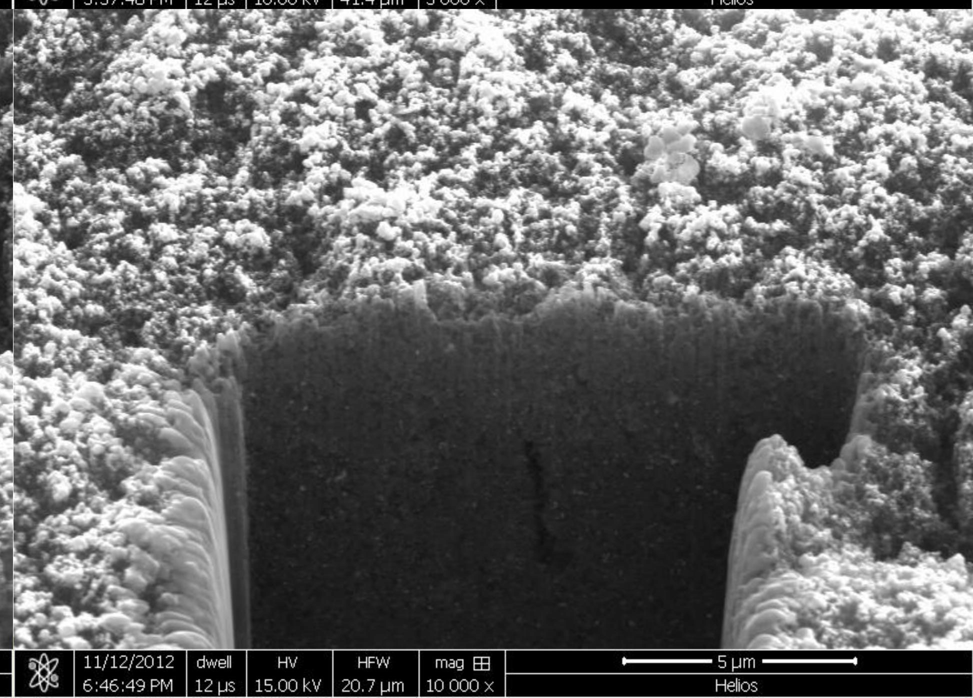

11/12/2012
3:14:05 PM
dwell
12 µs
HV
10.00 kV
HFW
5.18 µm
mag ⊞
40 000 x
2 µm
Helios

Pt/C 50k cyc


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
3:37:48 PM
dwell
12 µs
HV
10.00 kV
HFW
41.4 µm
mag
5 000 x
10 µm
Helios


11/12/2012
6:36:52 PM
dwell
12 µs
HV
15.00 kV
HFW
20.7 µm
mag
10 000 x
5 µm
Helios


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

Pt/C 50k cyc

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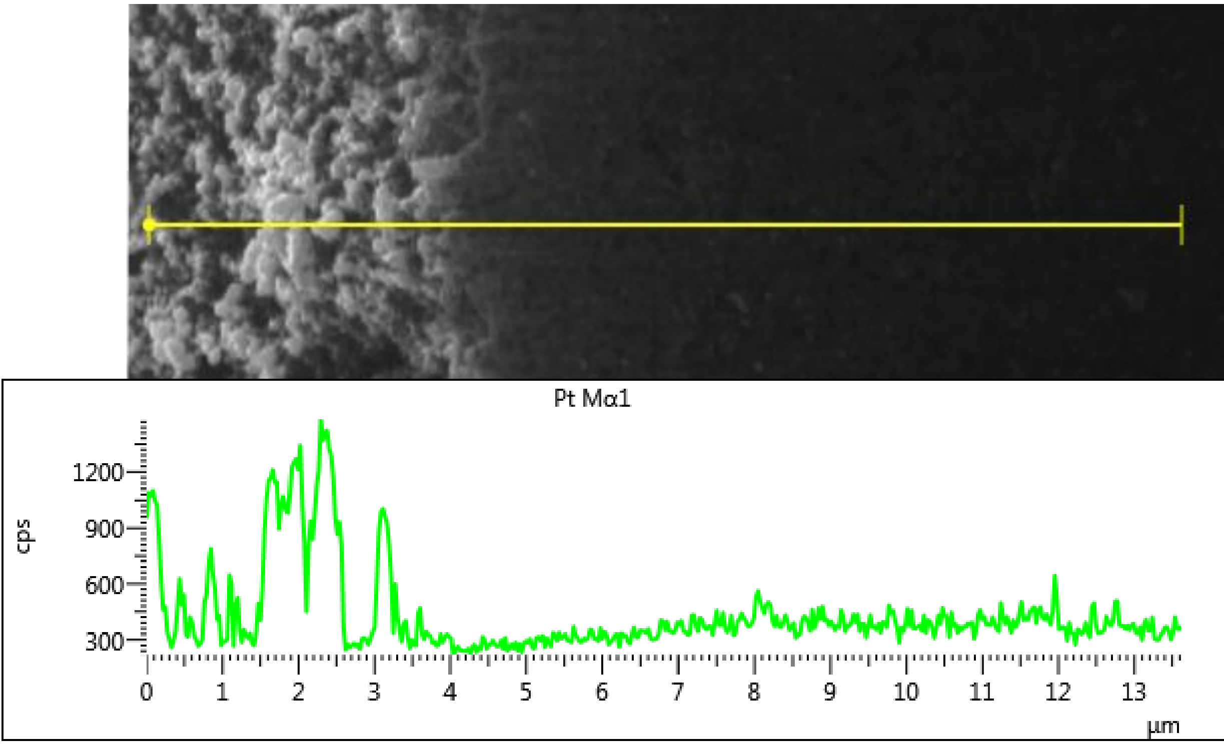

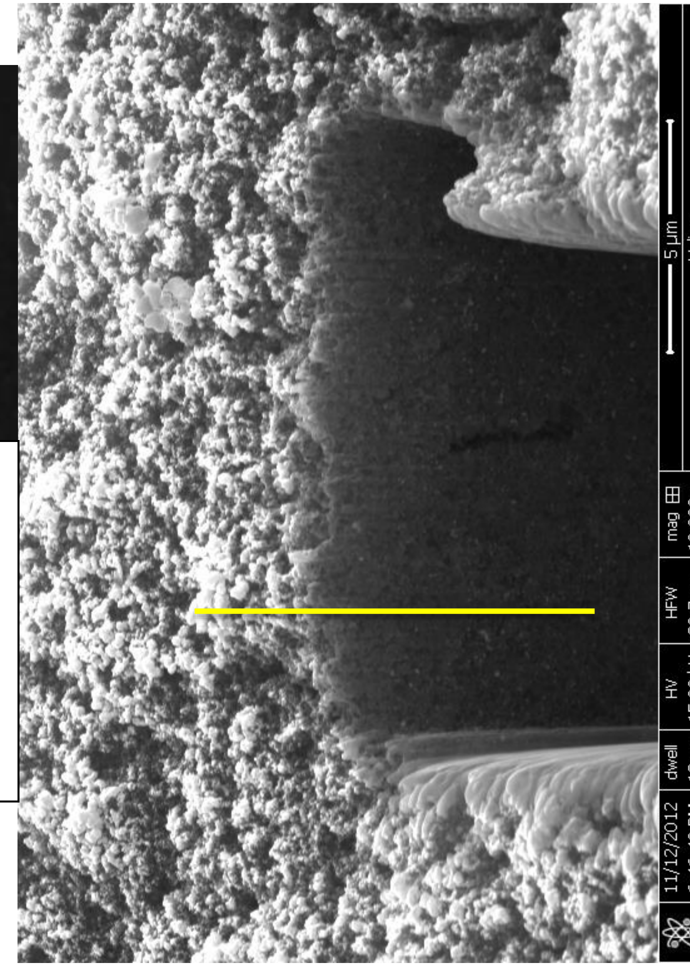

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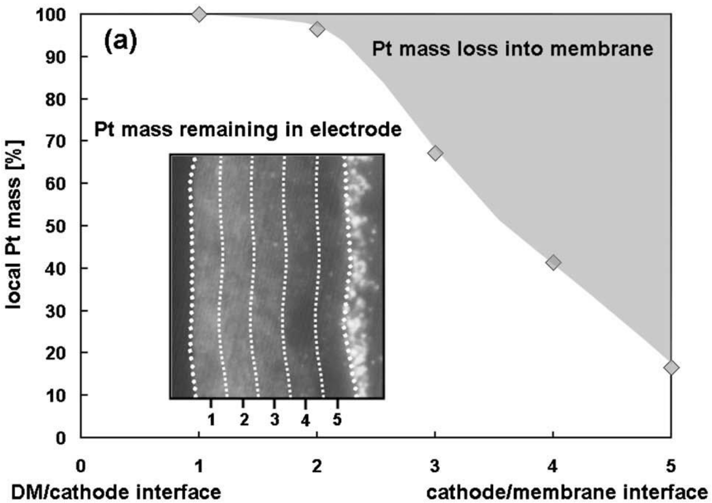
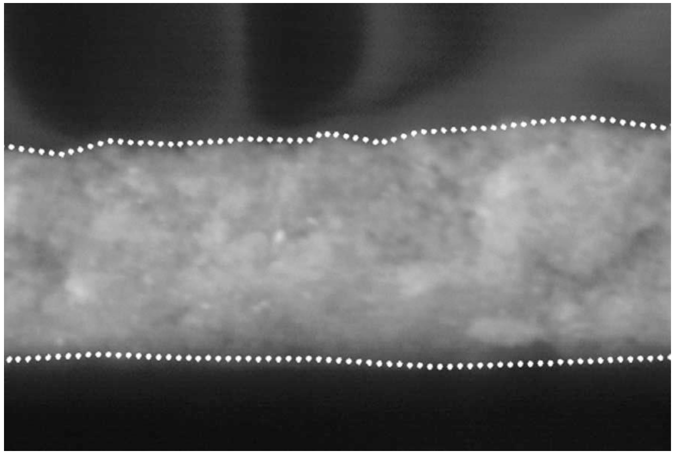
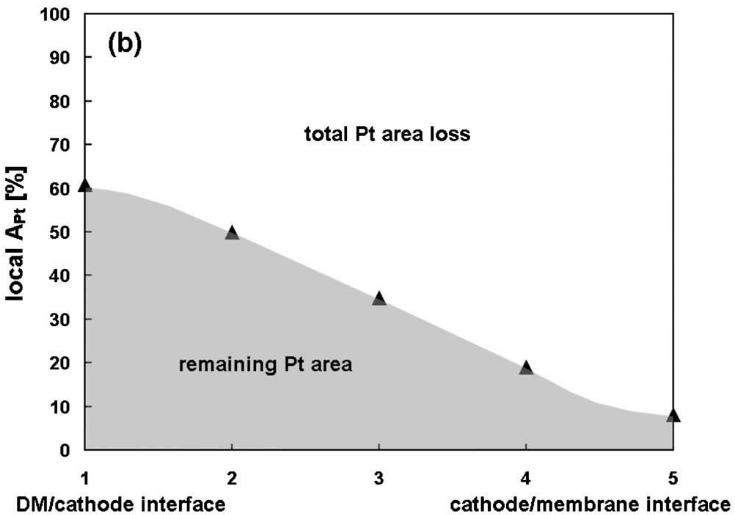
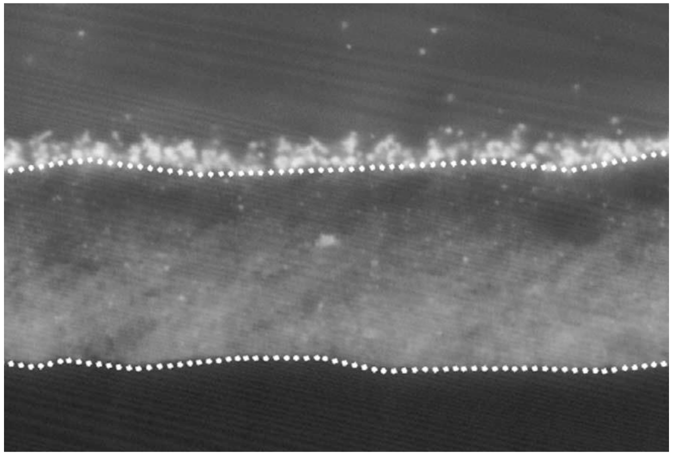
2010_Gasteiger_Shao_Platinum-Alloy Cathode Catalyst Degradation in Proton Exchange Membrane Fuel Cells: Nanometer-Scale Compositional and Morphological Changes

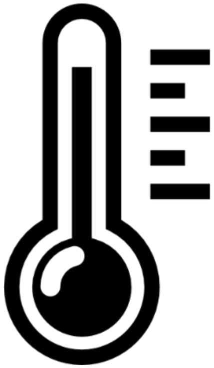








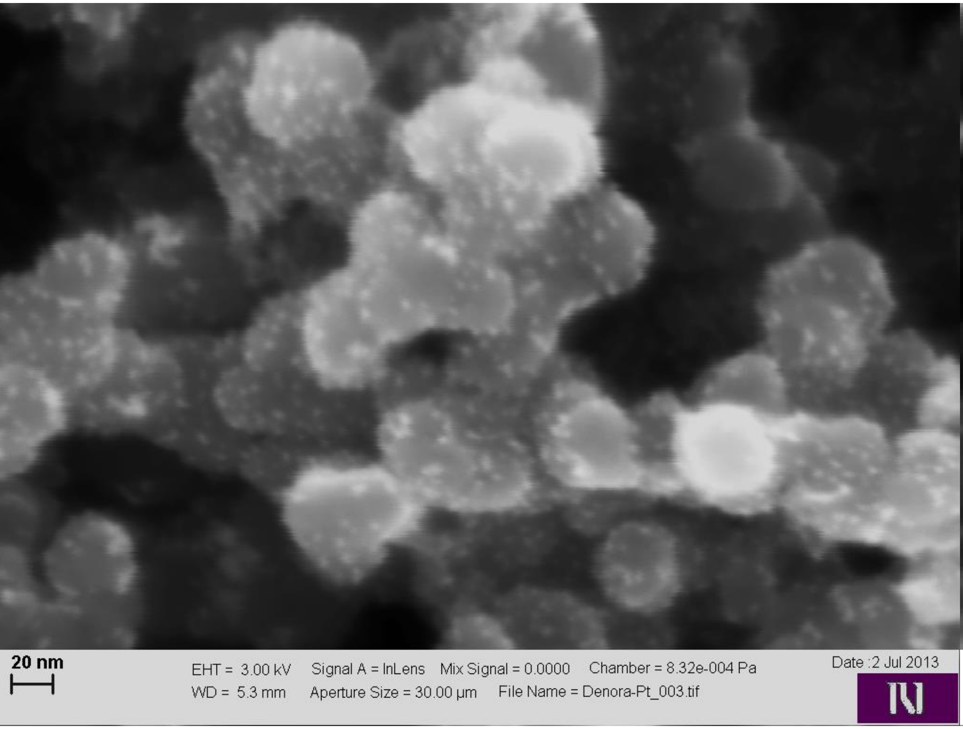
Effect of temperature

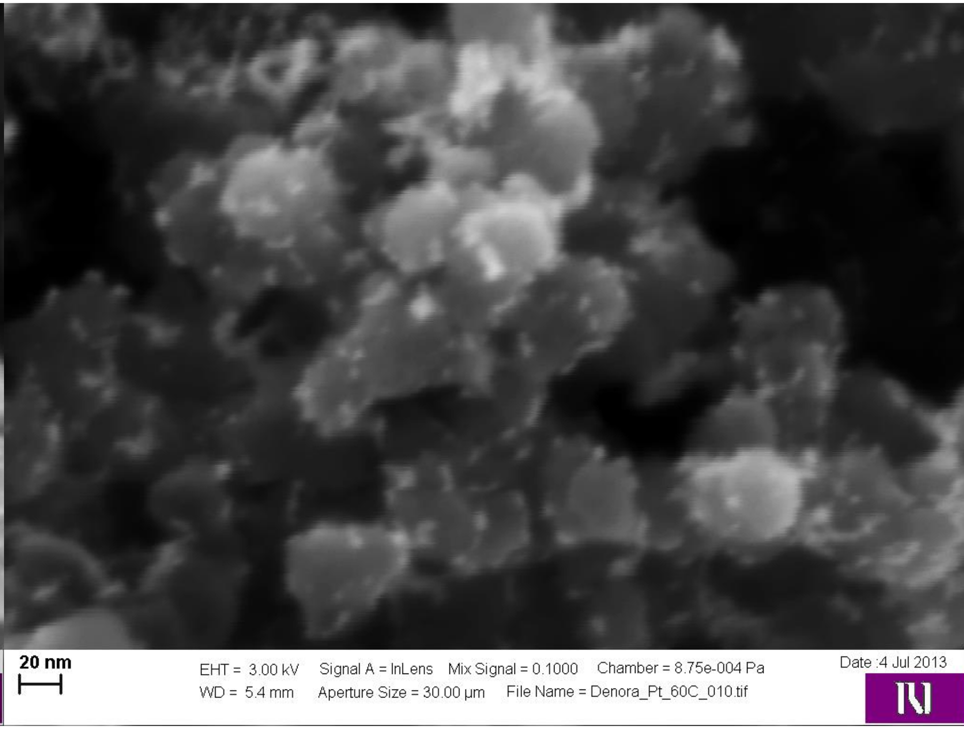


Before

After 60 °C at 1.4 V for 640 min

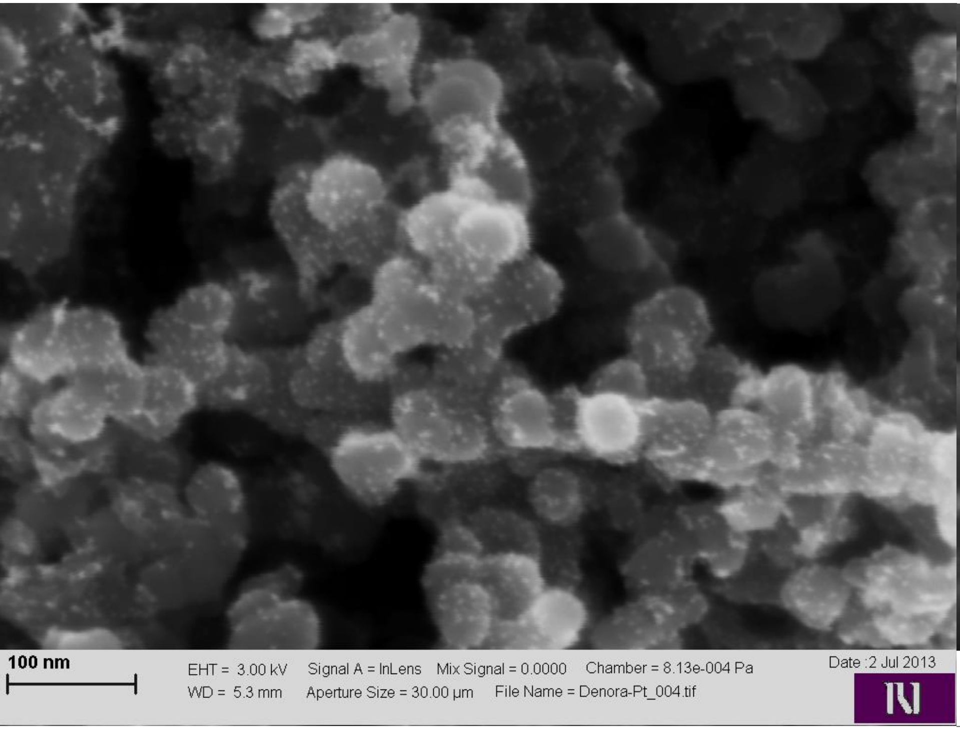
Zorko, *Ultramicroscopy*, **2014,** 140, 44–50

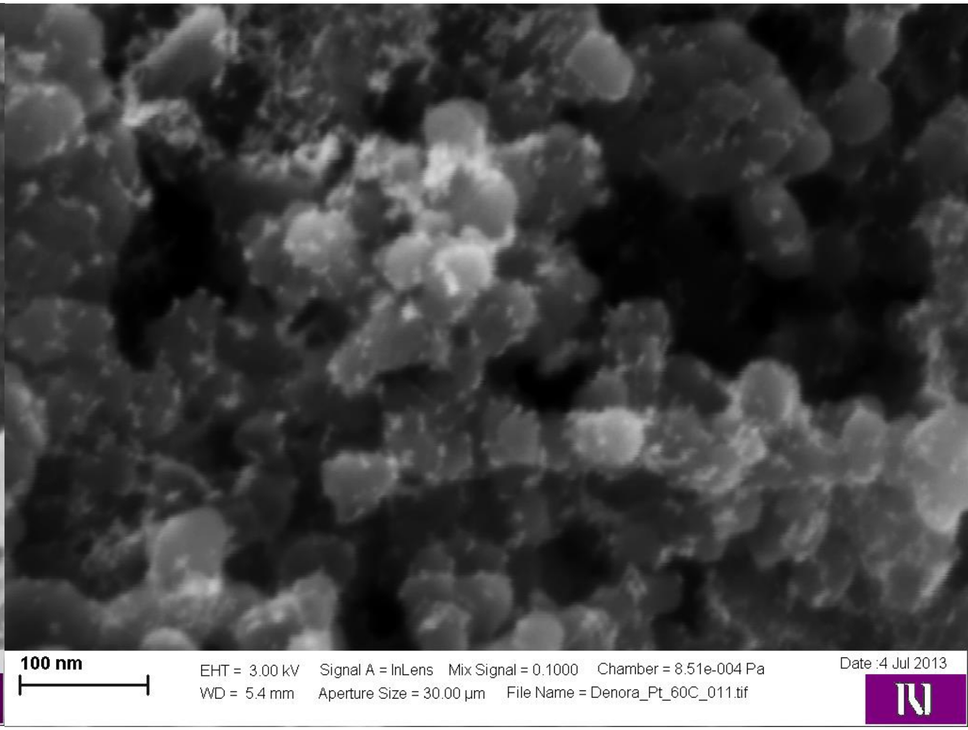




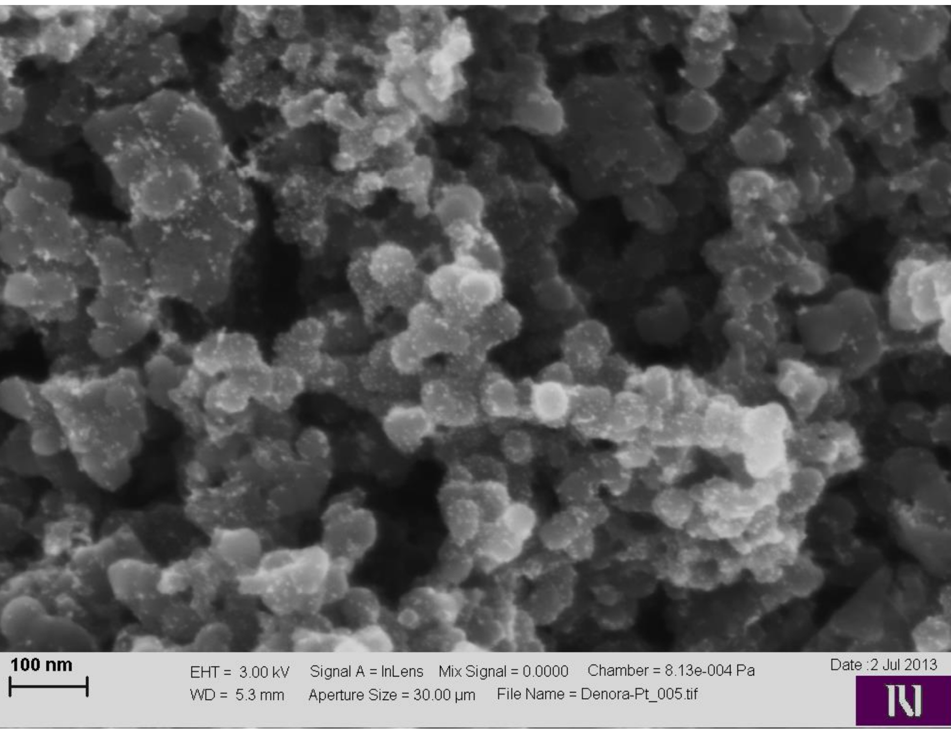
Zorko, *Ultramicroscopy*, **2014,** 140, 44–50

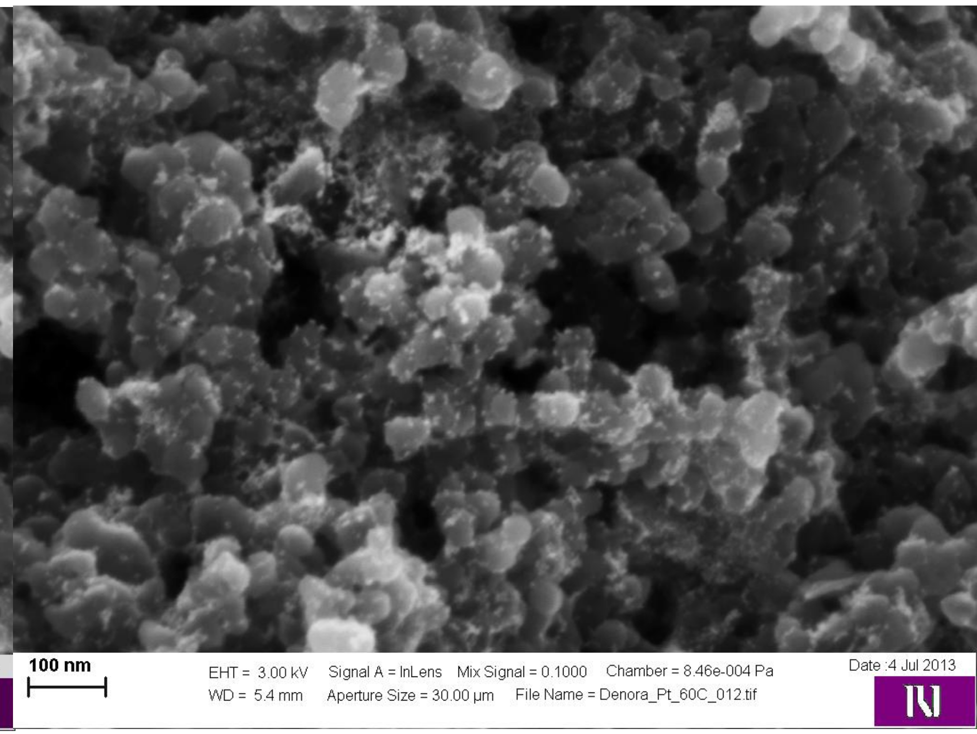
Univerza v Novi Gorici, Dvorec Lanthieri, 20.2.2020



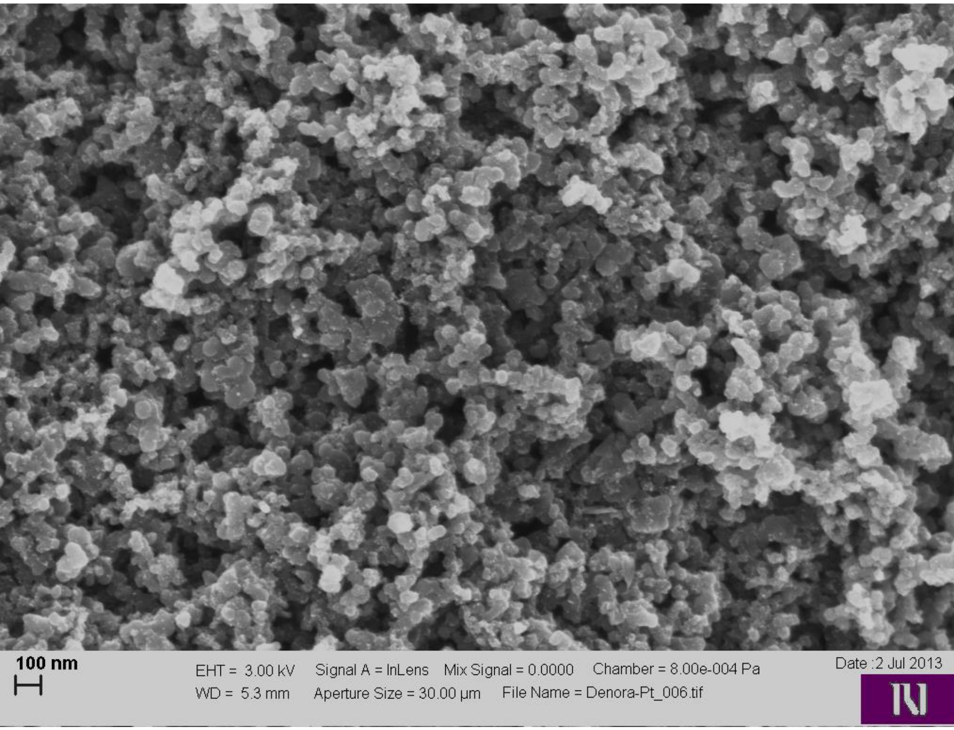


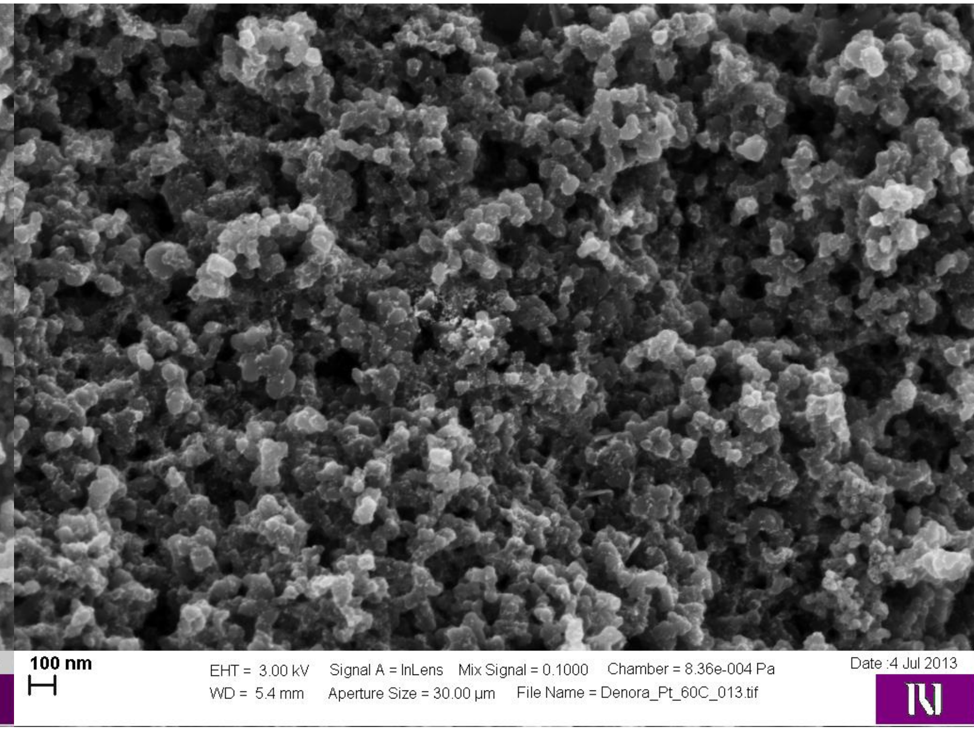
Univerza v Novi Gorici, Dvorec Lanthieri, 20.2.2020





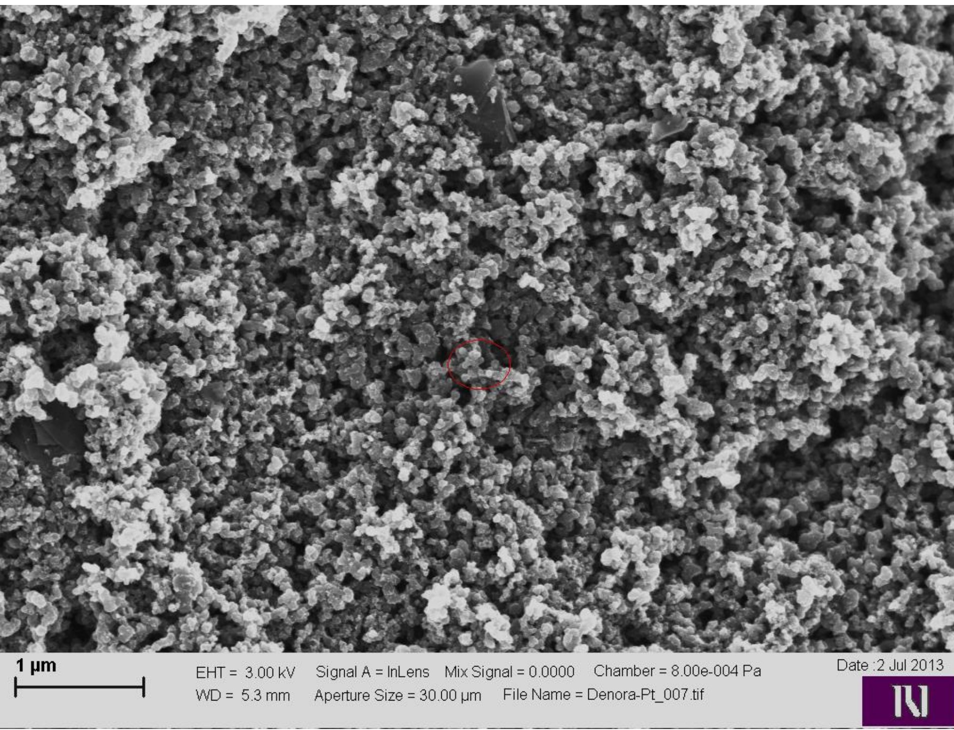
Zorko, *Ultramicroscopy*, **2014,** 140, 44–50

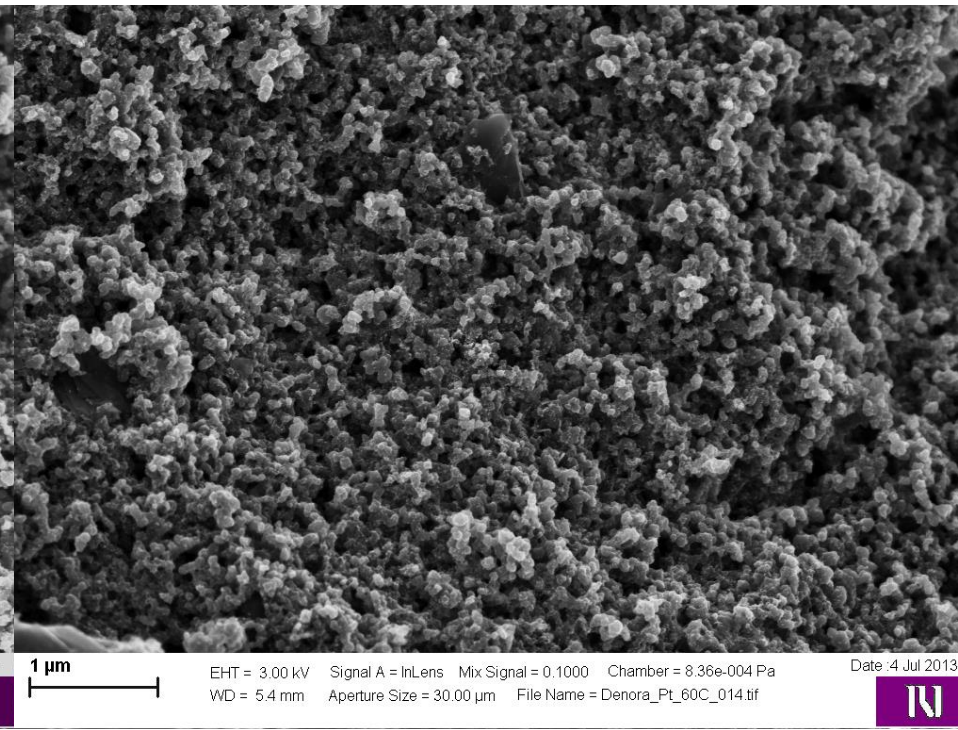




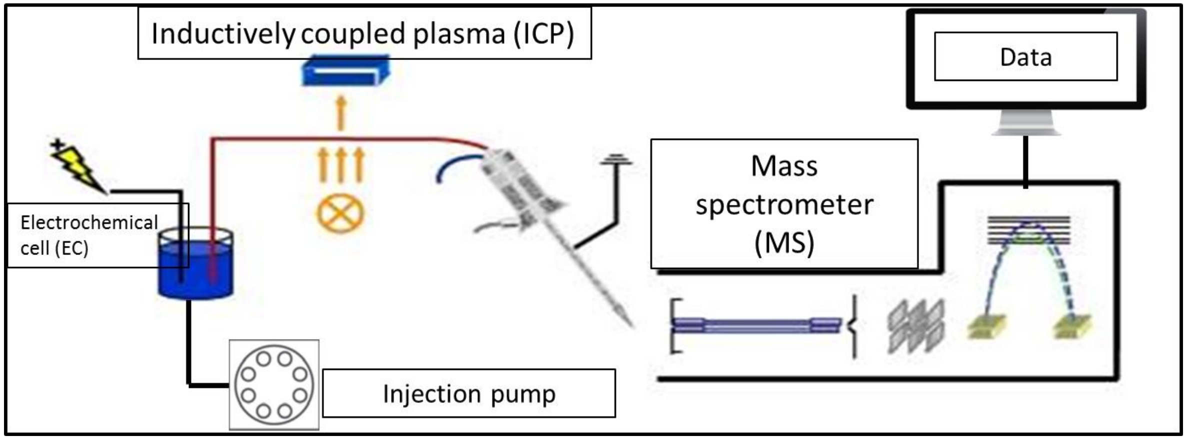
Zorko, *Ultramicroscopy*, **2014,** 140, 44–50

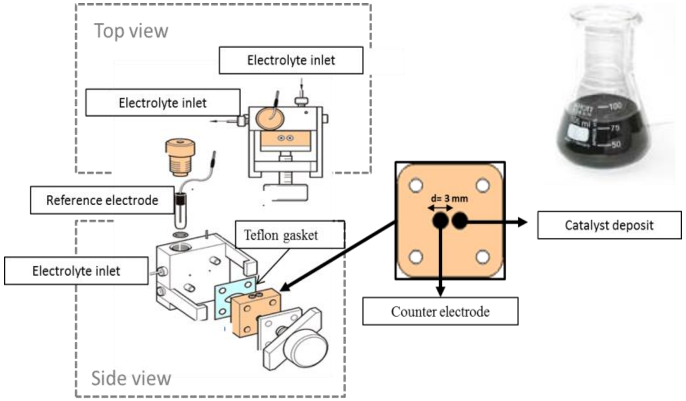
Univerza v Novi Gorici, Dvorec Lanthieri, 20.2.2020



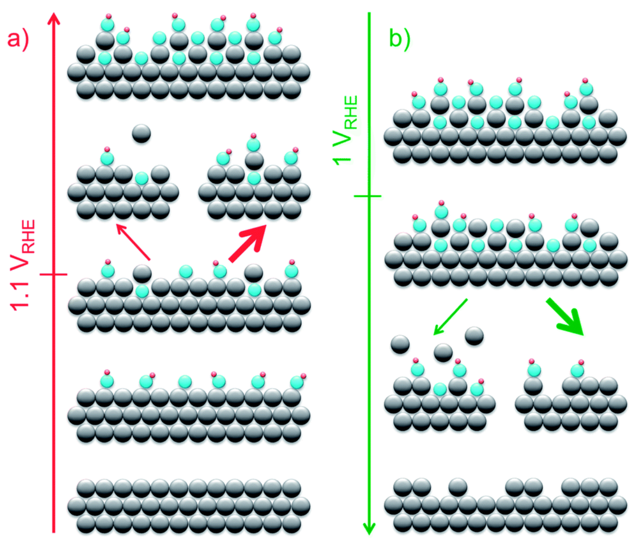


Electrocatalyst online dissolution - ICP-MS

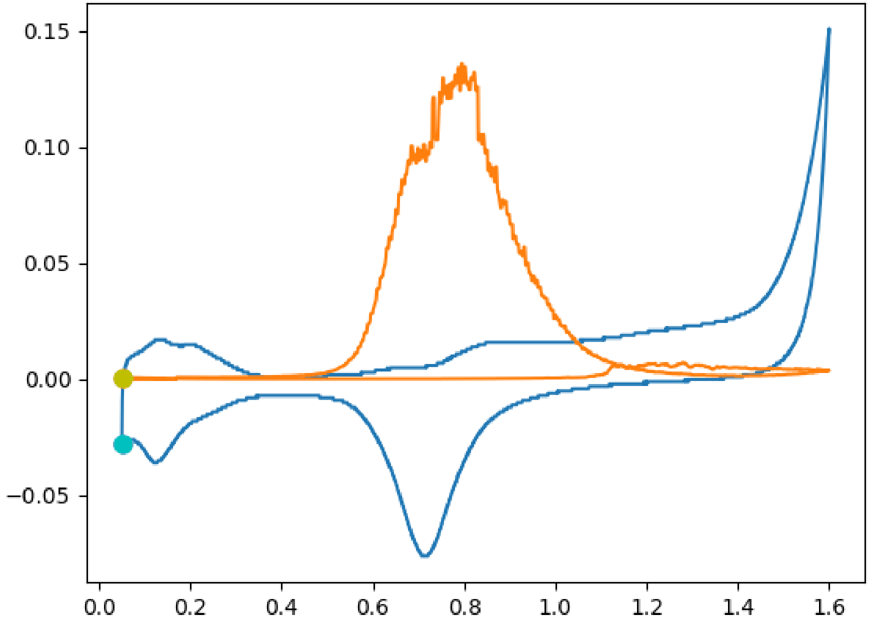




Information on sub-monolayer bulk stability



Chem. Sci., 2014, 5, 631-638

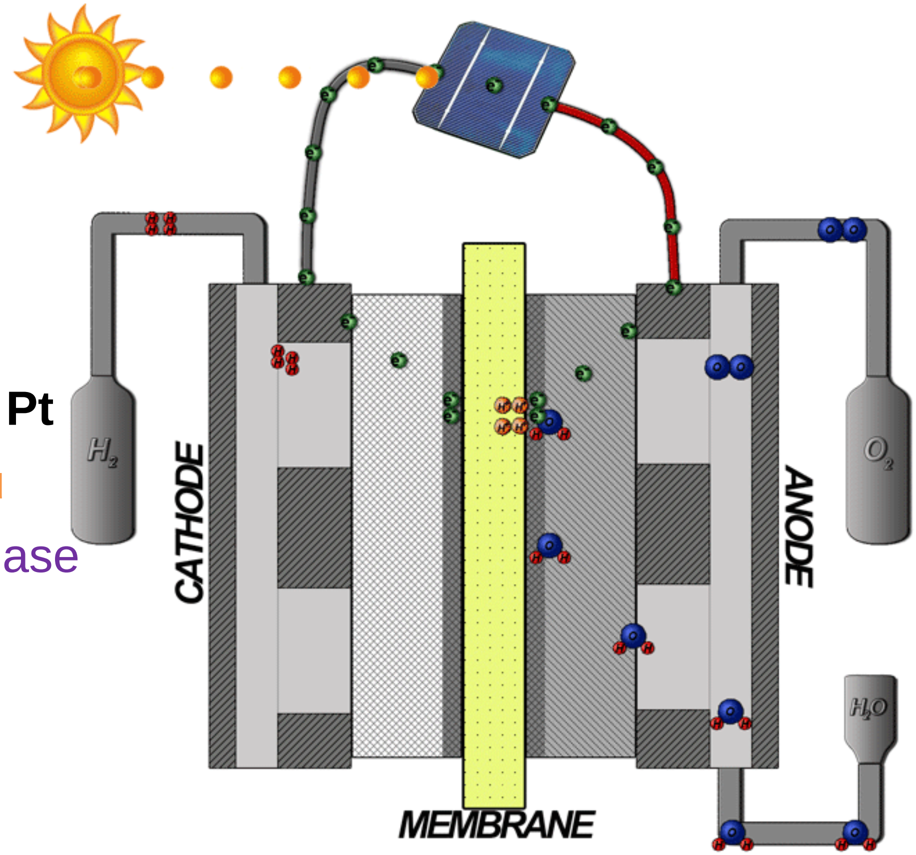


Proton exchange membrane electrolyzer

Hydrogen evolution - **Pt**

CO_2 redcution - **Cu**

N_2 redcution - nitrogenase

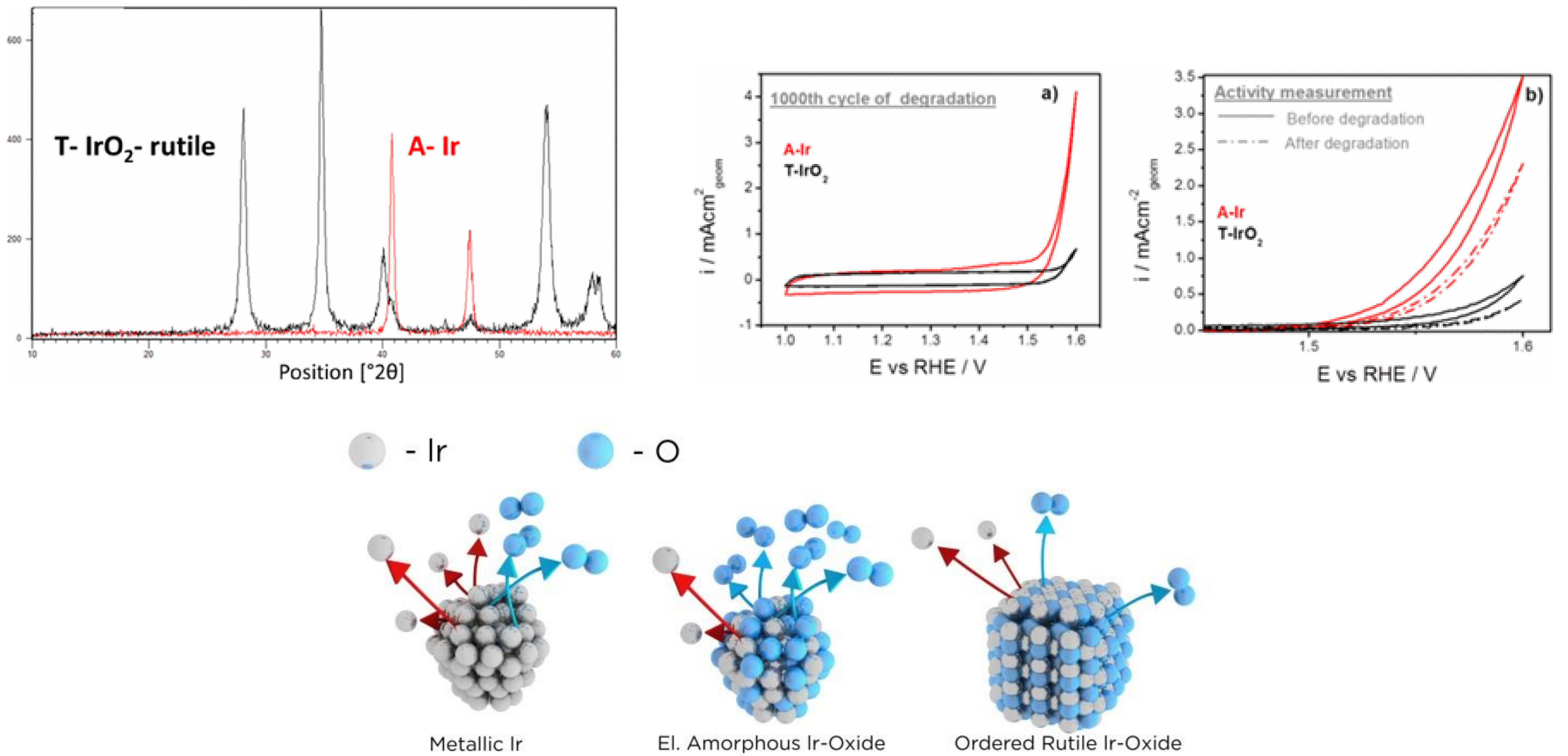


Oxygen evolution - **Ir**

https://en.wikipedia.org/wiki/Polymer_electrolyte_membrane_electrolysis

Degradation at high oxidative potentials?

Ir-black, electrocatalyst for oxygen evolution reaction



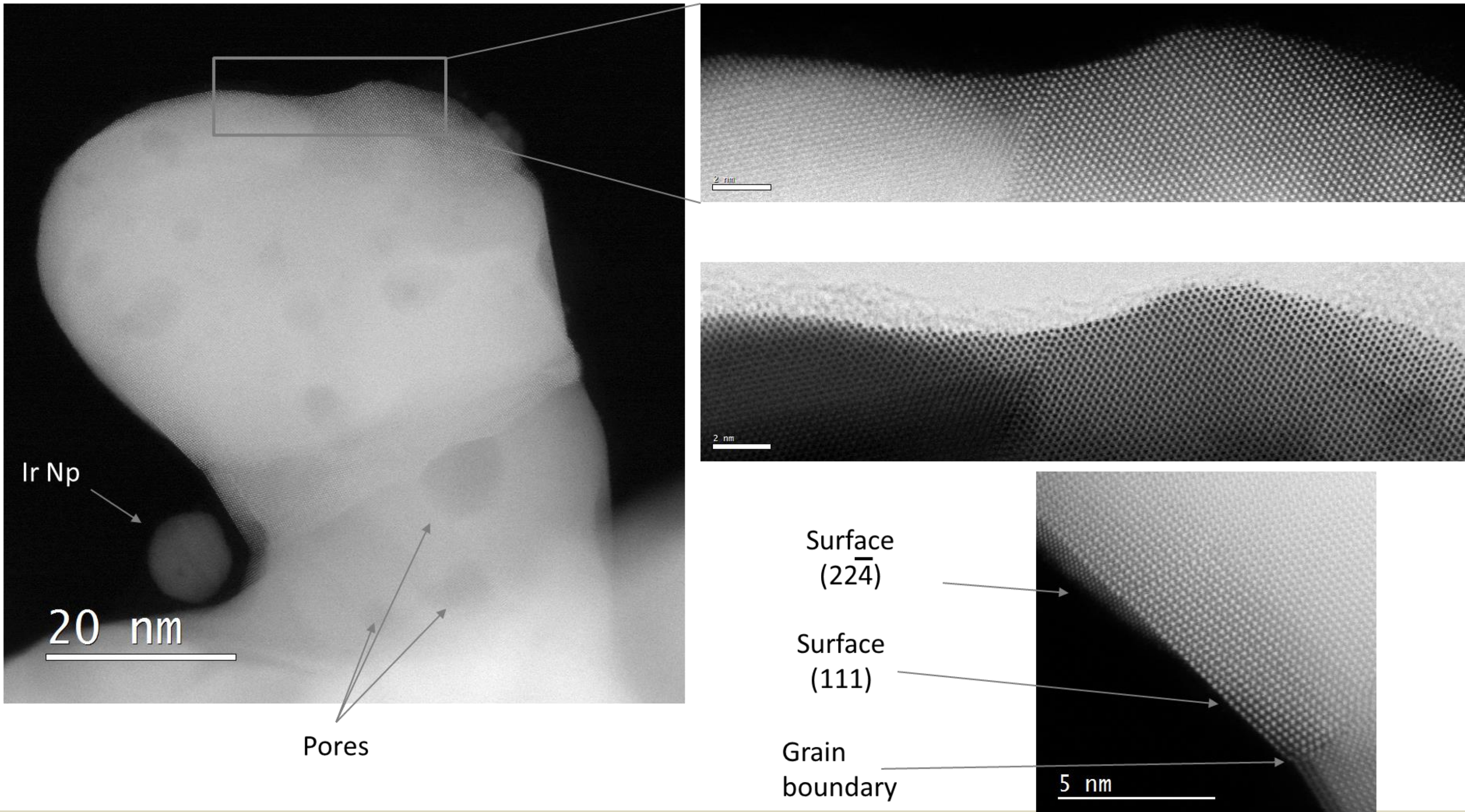
Degradation at high oxidative potentials?

Ir-black, electrocatalyst for oxygen evolution reaction

Jovanovič, J. Am. Chem. Soc. 2017, 139, 12837–12846.

Univerza v Novi Gorici, Dvorec Lanthieri, 20.2.2020

Degradation at high oxidative potentials?

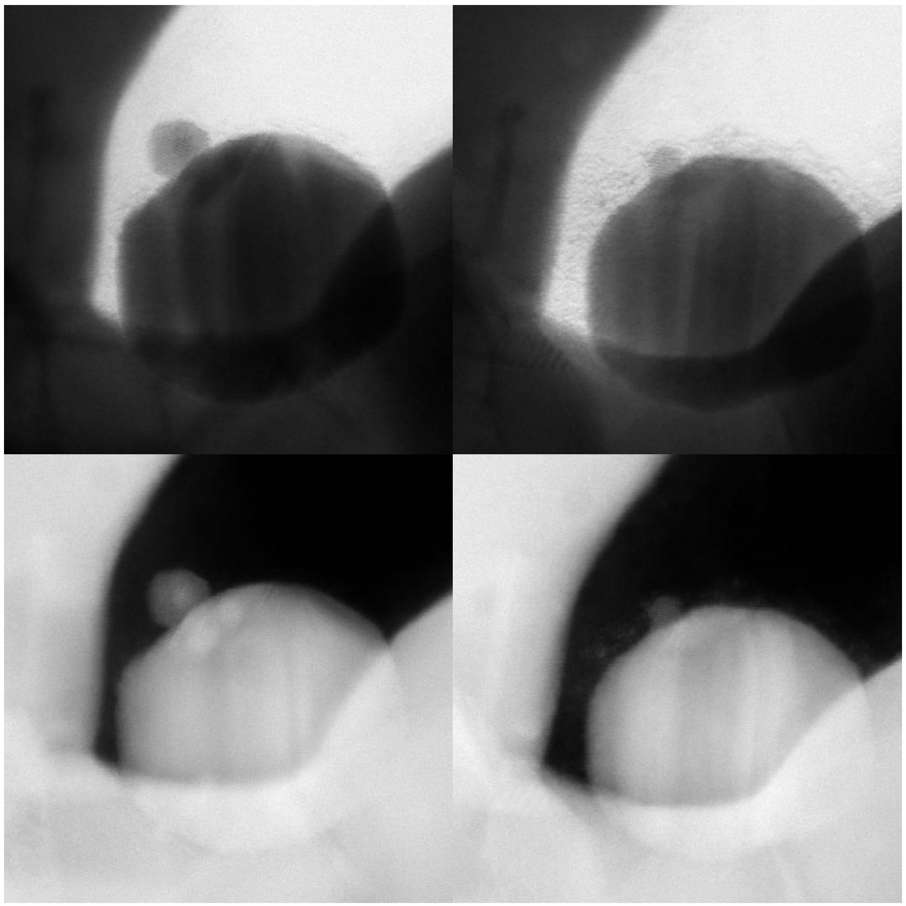


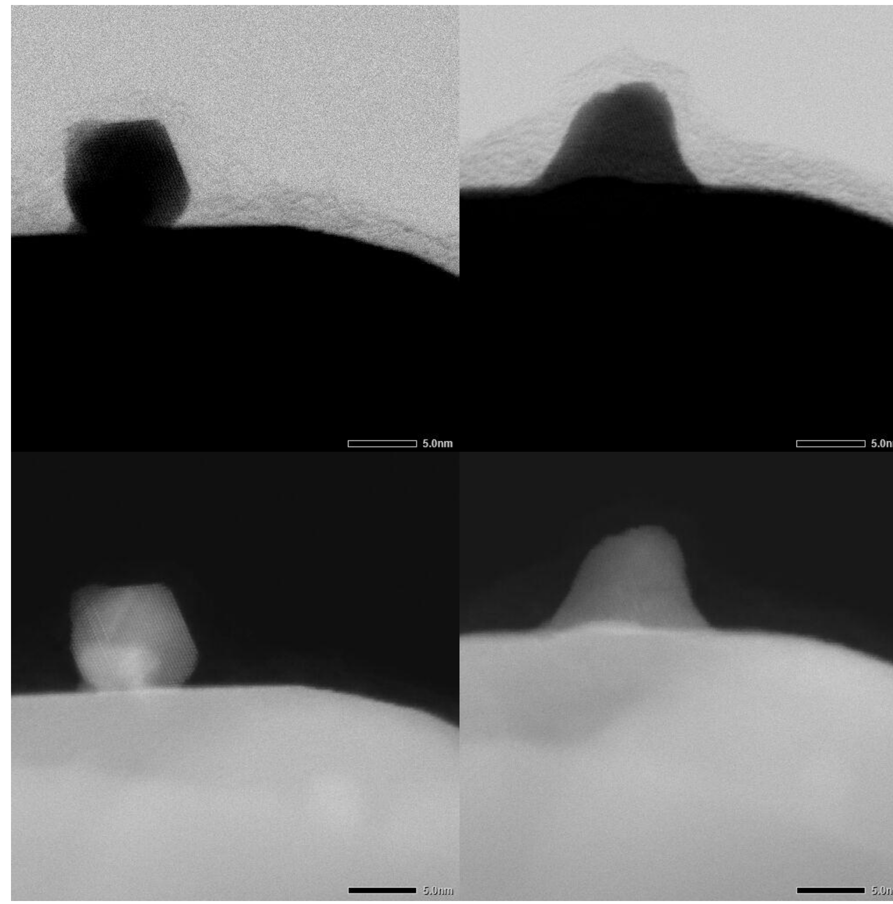
Jovanovič, J. Am. Chem. Soc. 2017, 139, 12837–12846.

Degradation at high oxidative potentials?

Ir-black, electrocatalyst for oxygen evolution reaction

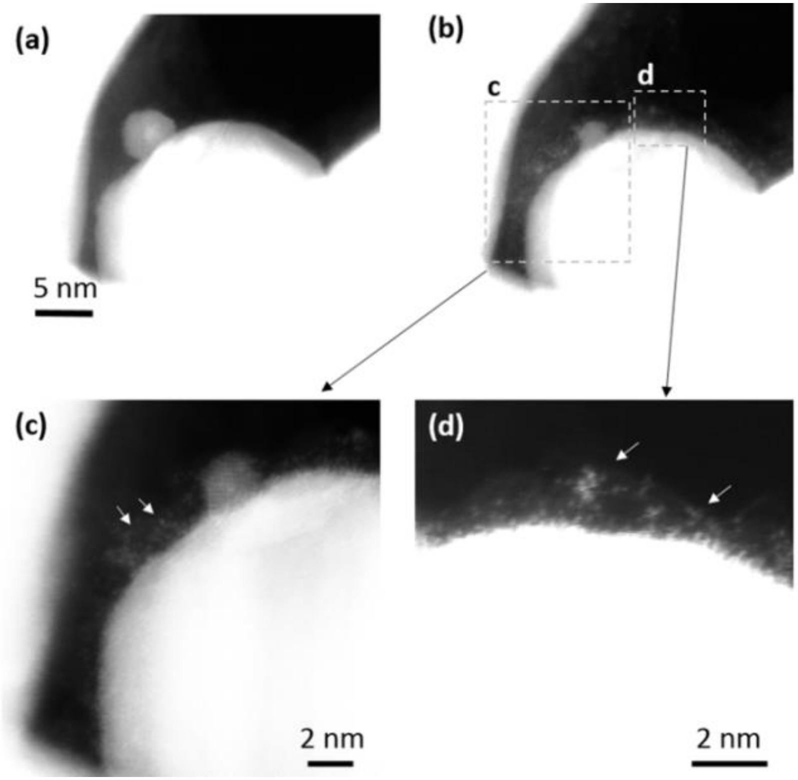
Degradatoion if Ir *via* dissolution: **0, 5000**, 10000, 15000 cycles



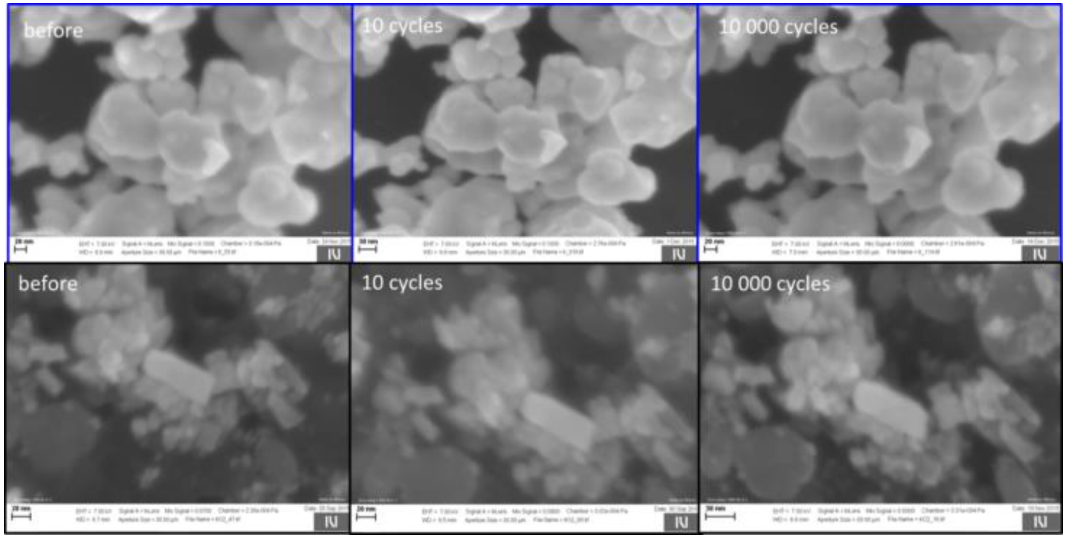


Degradation at high oxidative potentials?

Degradatoion if Ir *via* dissolution: 0, 5000, 10000, 15000 cycles



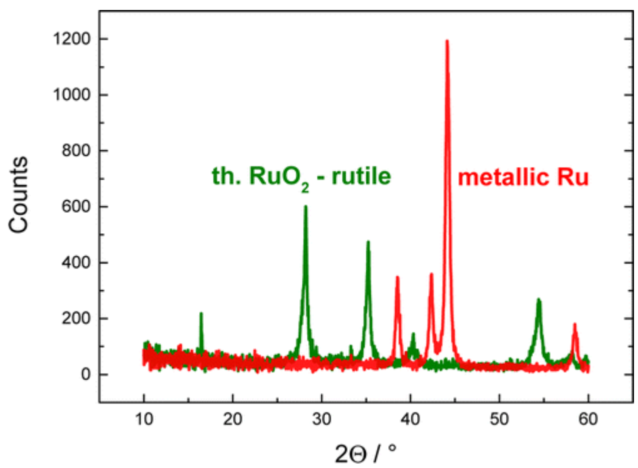
1-1.6 V

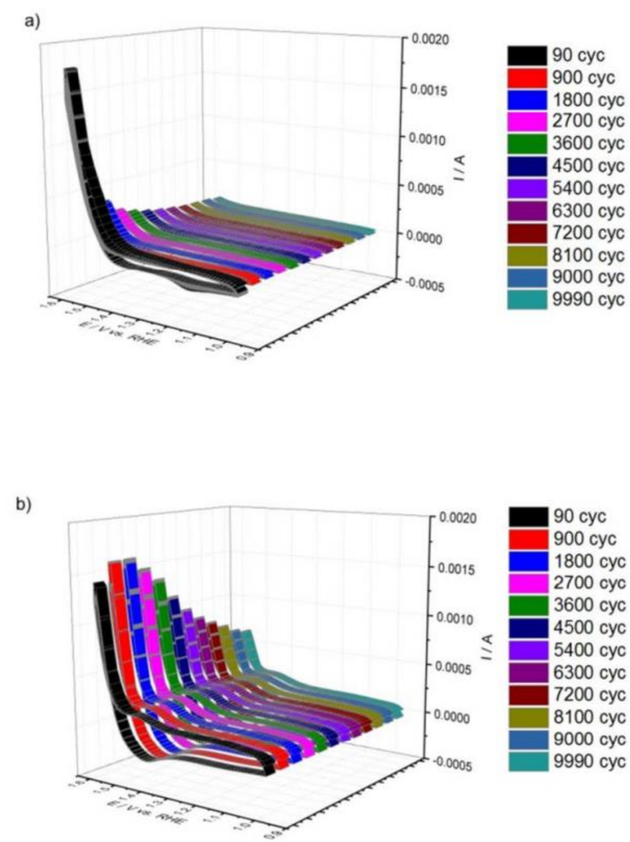


200 potential cycles between 0.05 and 1.2 V with a scan rate 300 mV s^{-1}

Degradation at high oxidative potentials?

Ru-black, highly active electrocatalyst for oxygen evolution reaction

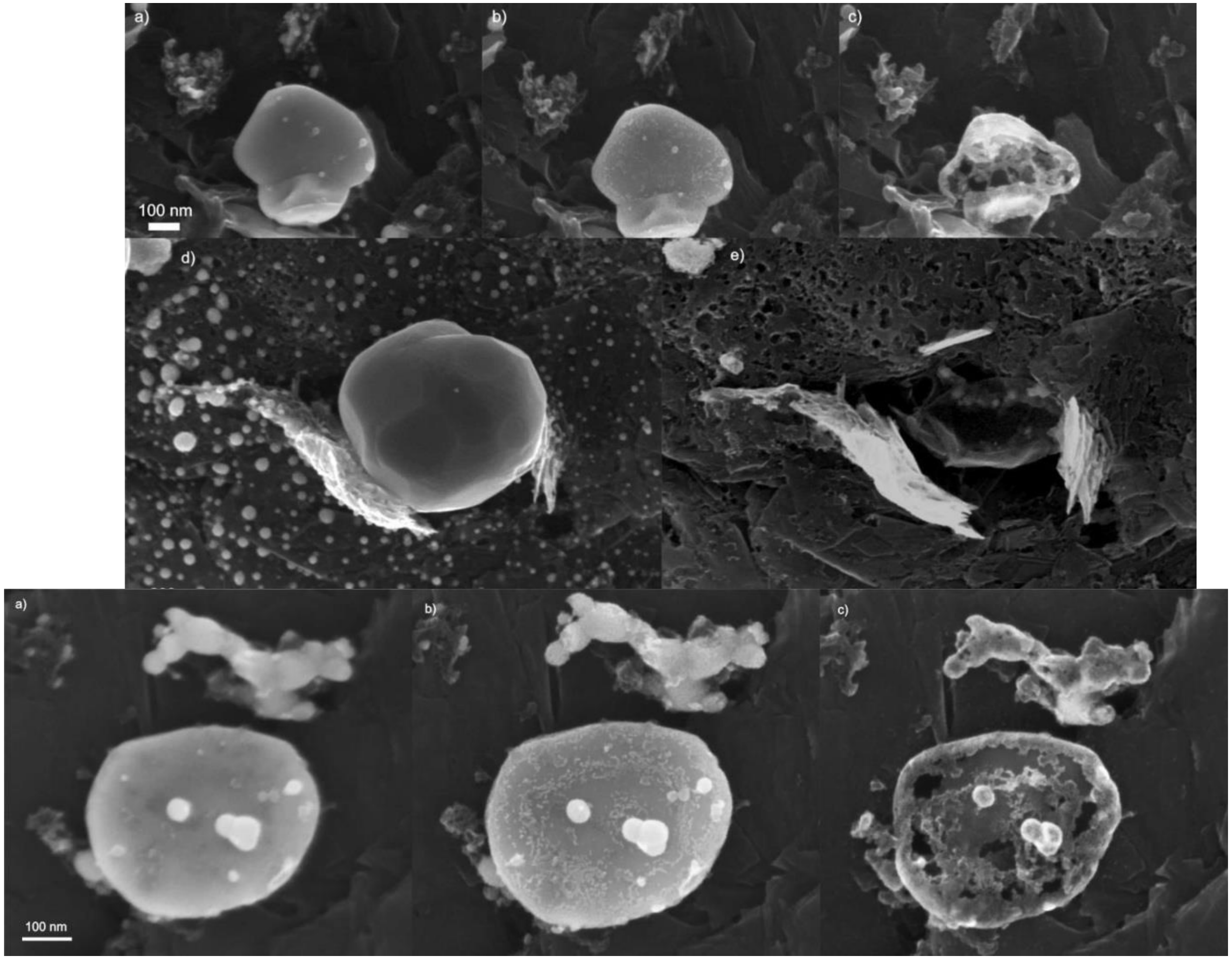




Not really stable

Degradation at high oxidative potentials?

Ru-black, highly active electrocatalyst for oxygen evolution reaction



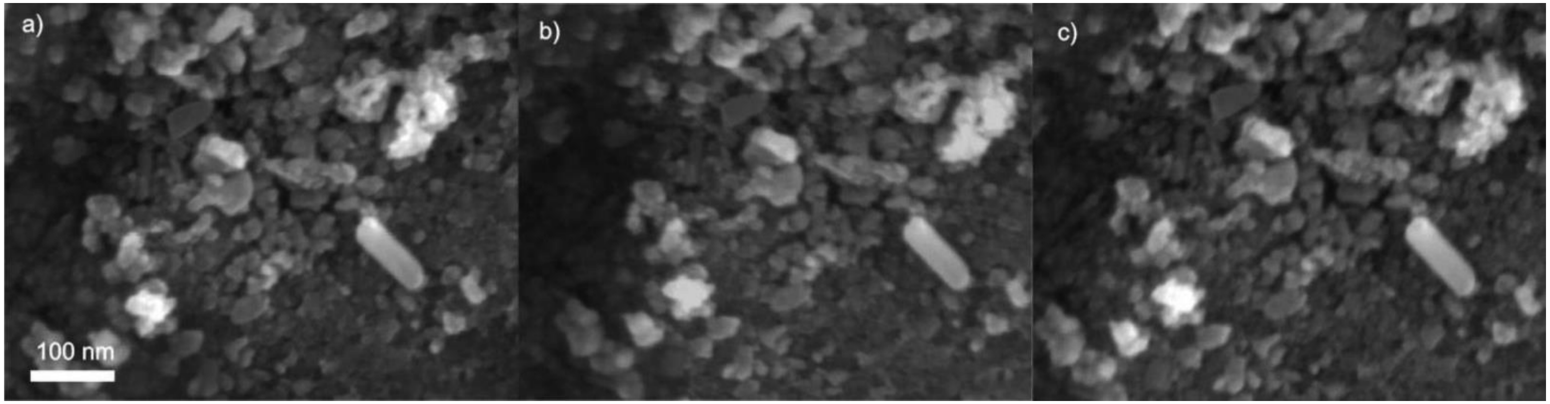
Hodnik, J. Phys. Chem. C 2015, 119, 18, 10140-10147

Degradation at high oxidative potentials?

Ru

RuO_2

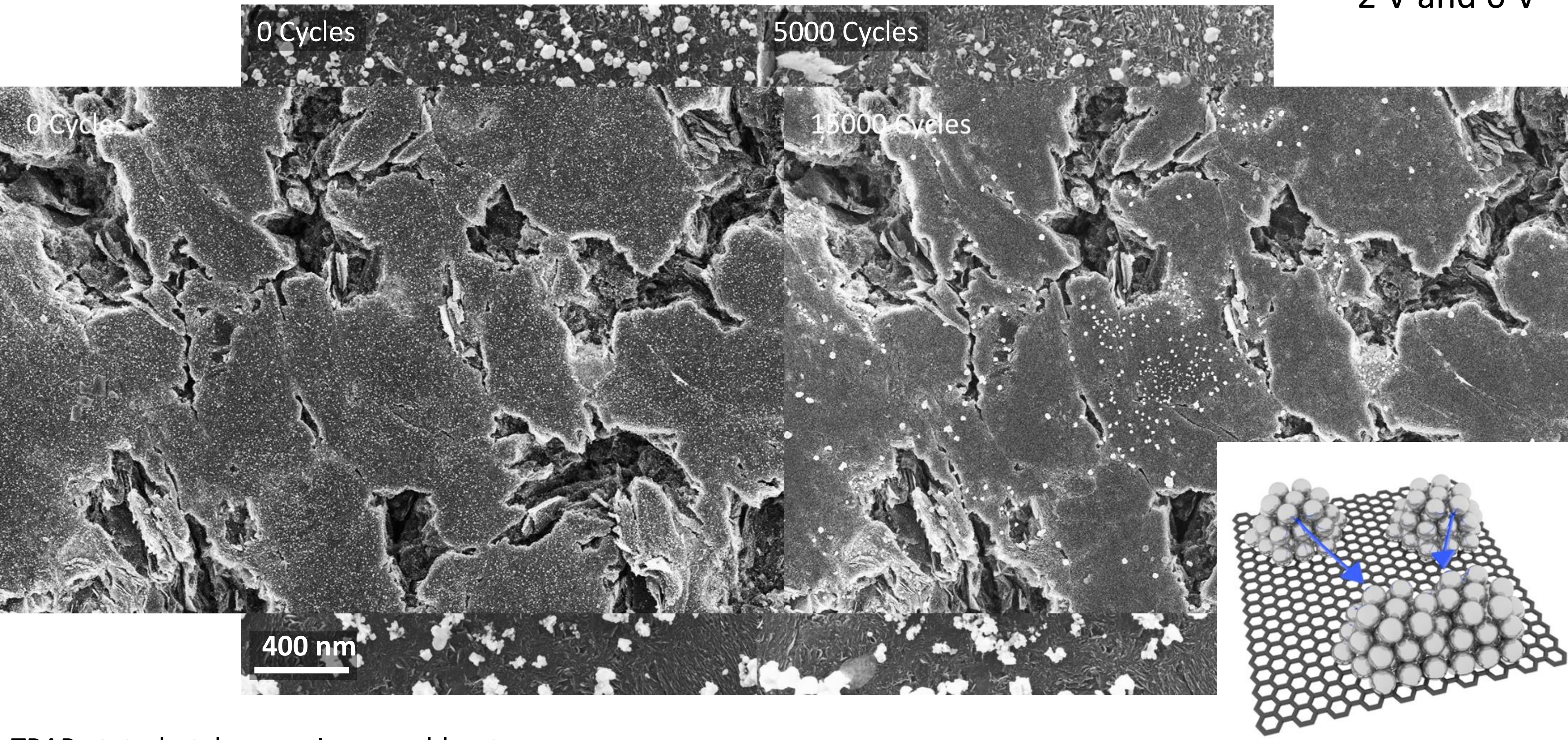
Cycling till 1,6 V *10th cycle* *10000 cycle*



What about degradation at reductive potentials?

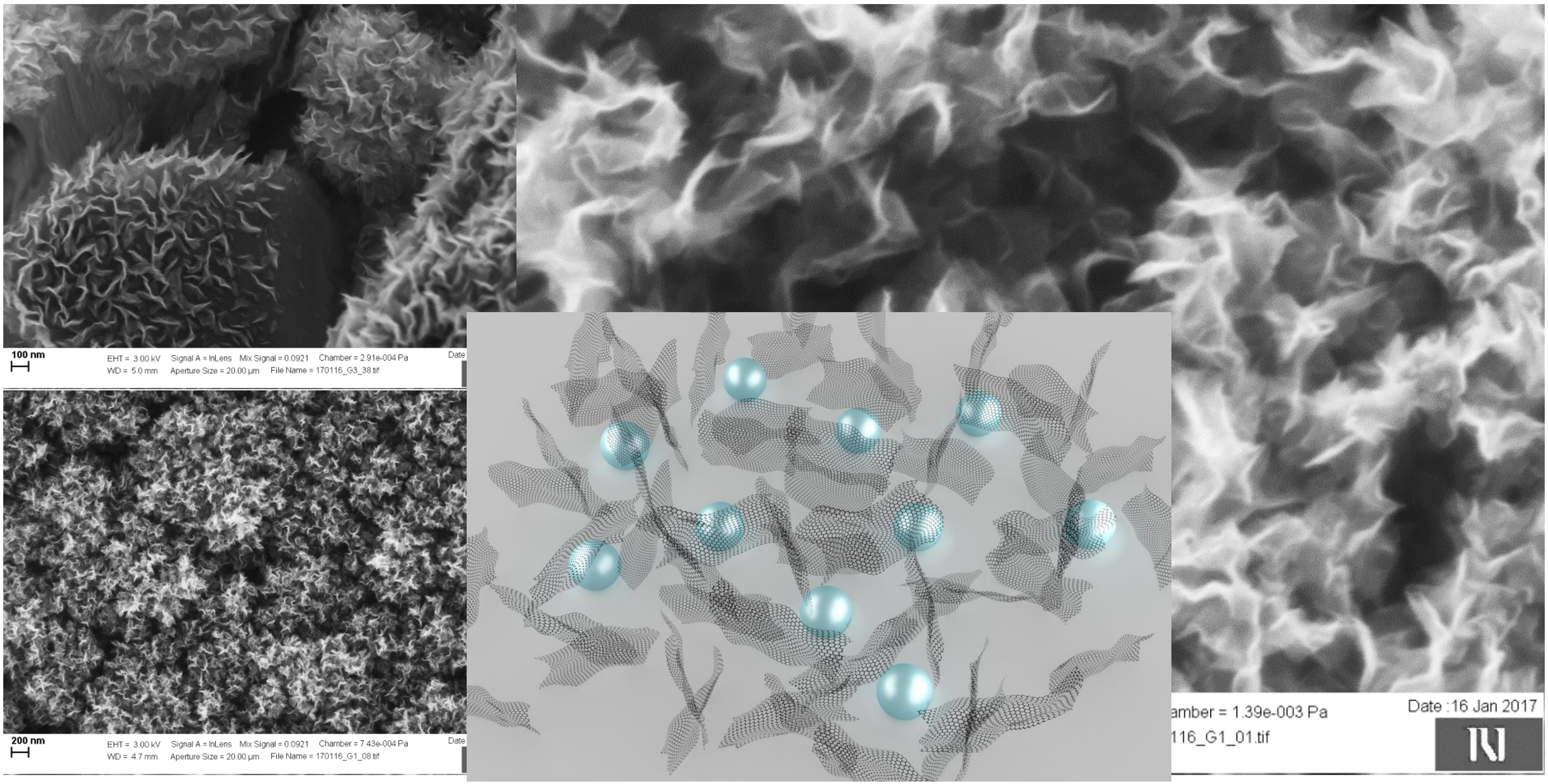
Degradatoion of Ag *via* coalesence: 0, 5000, 10000, 15000 cycles

-2 V and 0 V



TBAP - tetrabutylammonium perchlorate

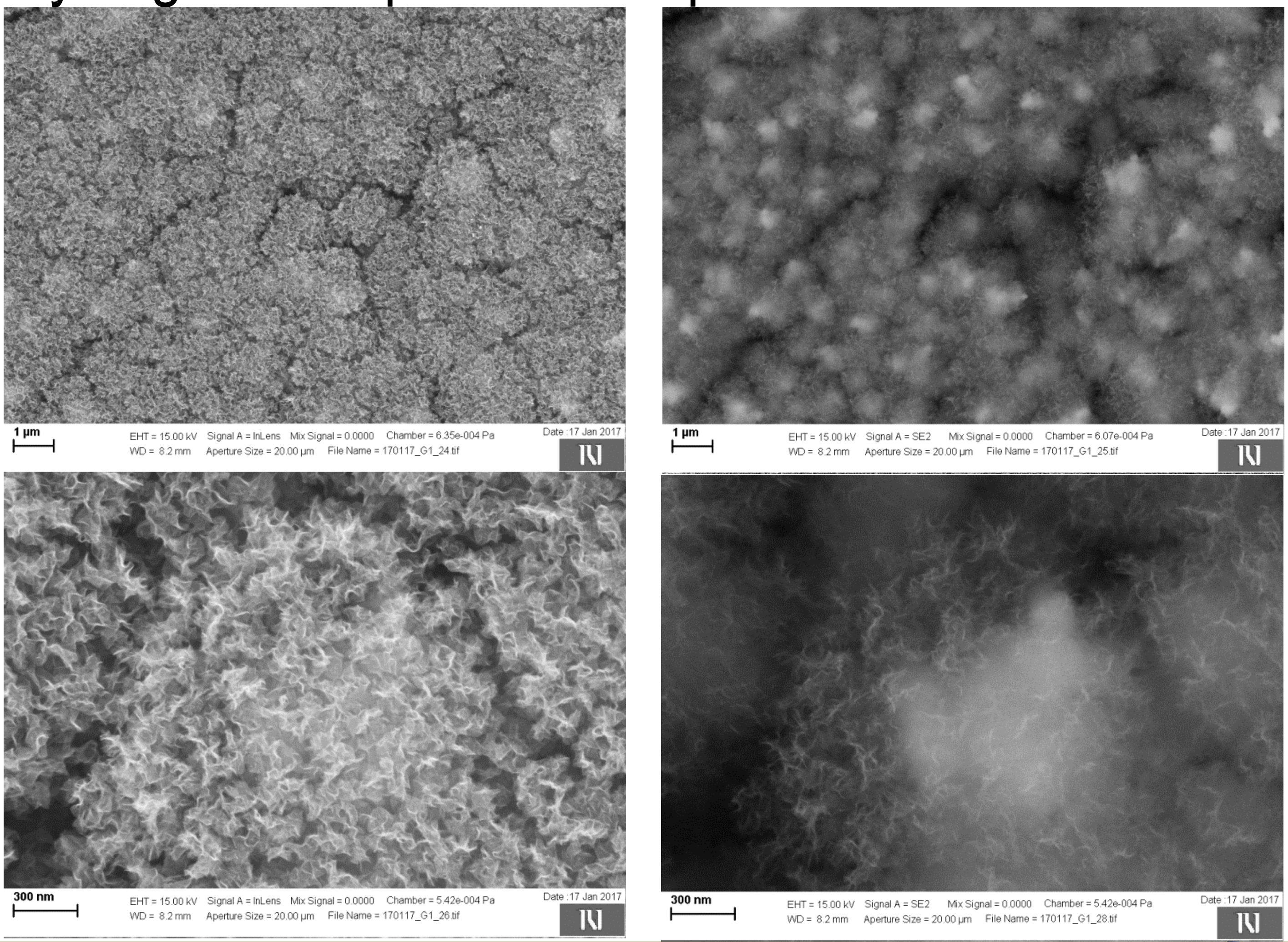
Plasma Grown Vertically Aligned Graphene



Vanrenterghrm, Chem. Comm., 2017,vol. 53, pp.9340-9343.

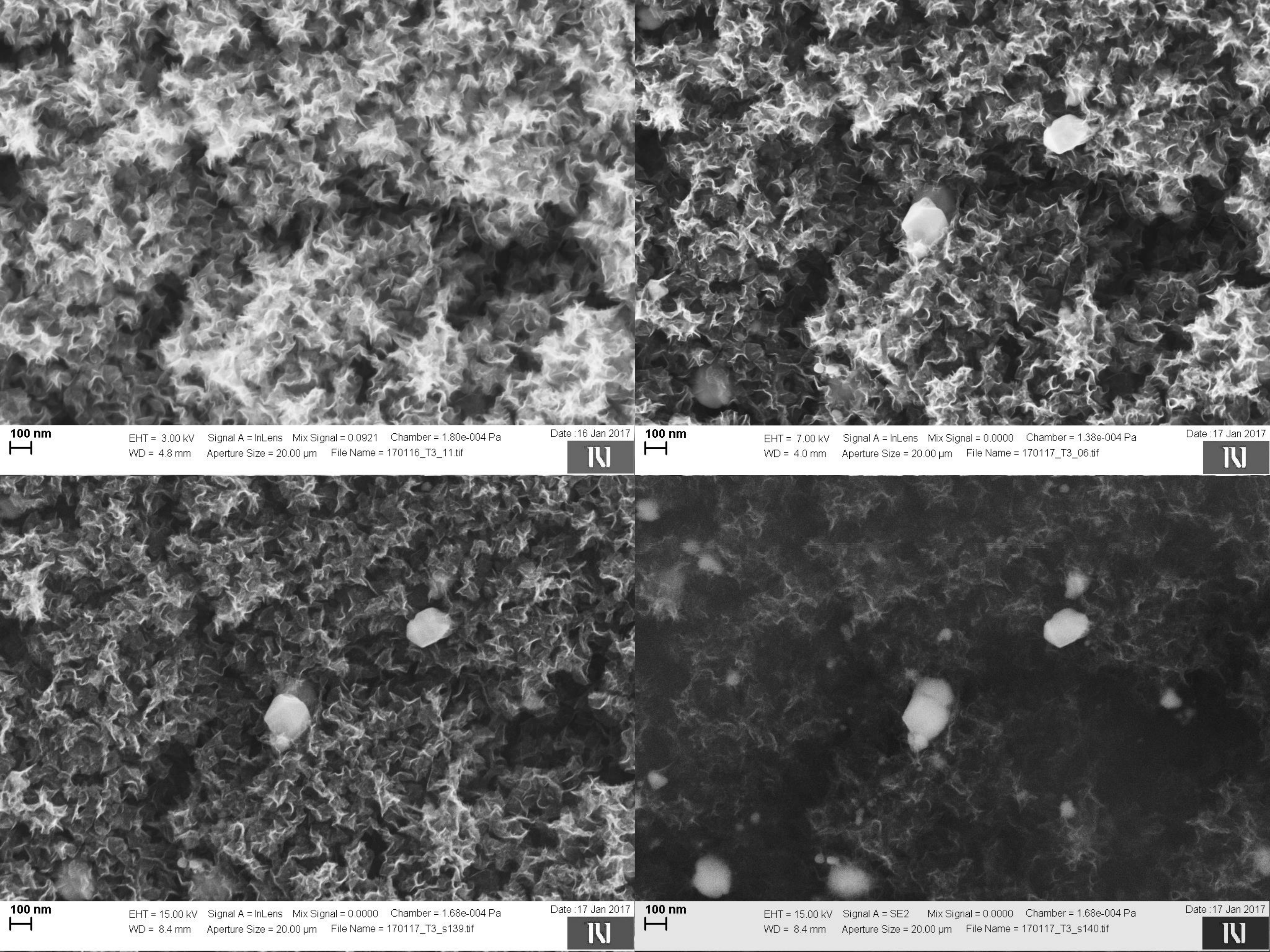
Increase of Electrodeposited Catalysts Stability *via* Plasma Grown Vertically Aligned Graphene Nanoparticles Movement Restriction!

in-lens detector

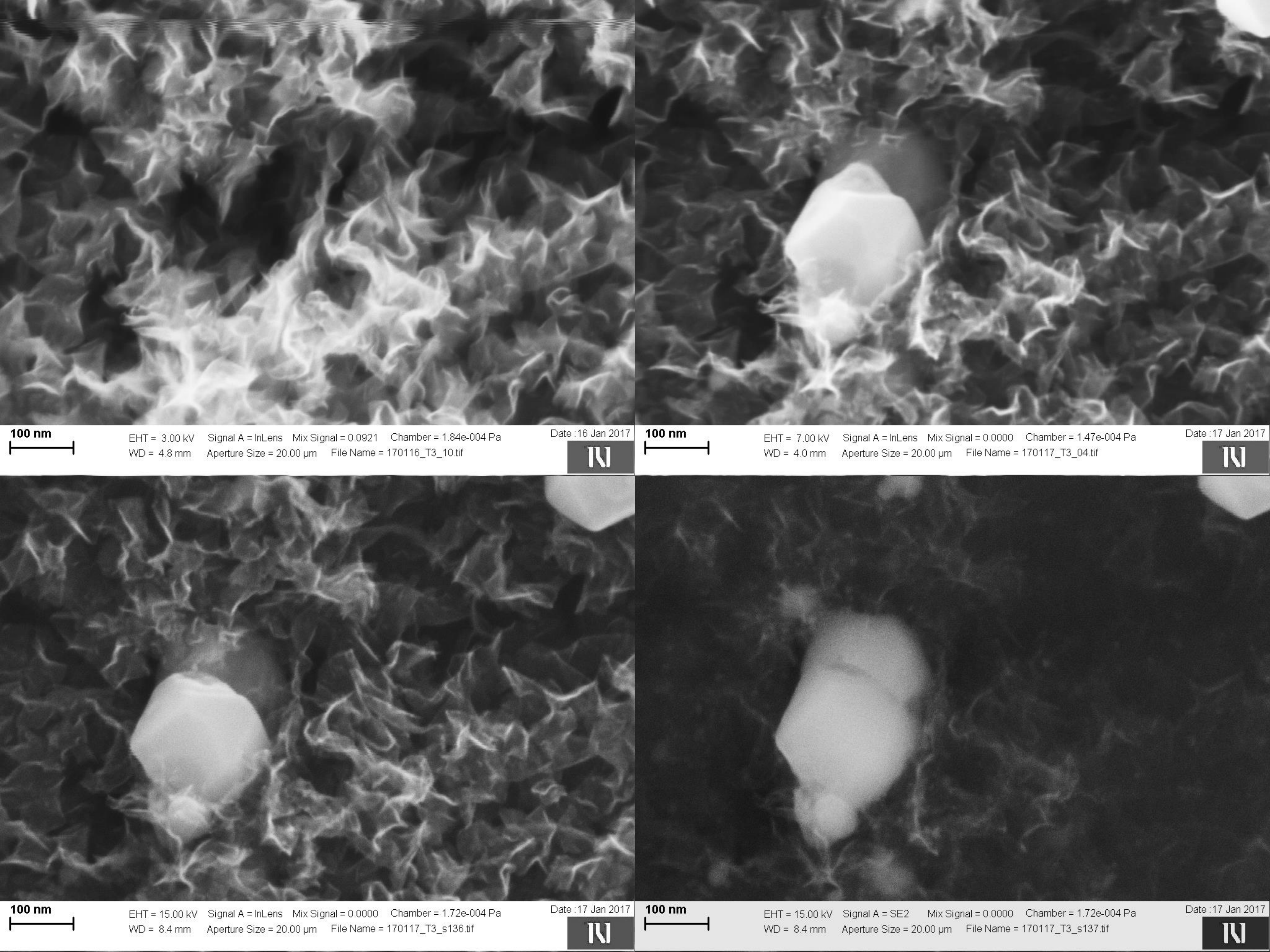


secondary electron detector

Vanrenterghrm, Chem. Comm., 2017,vol. 53, pp.9340-9343.

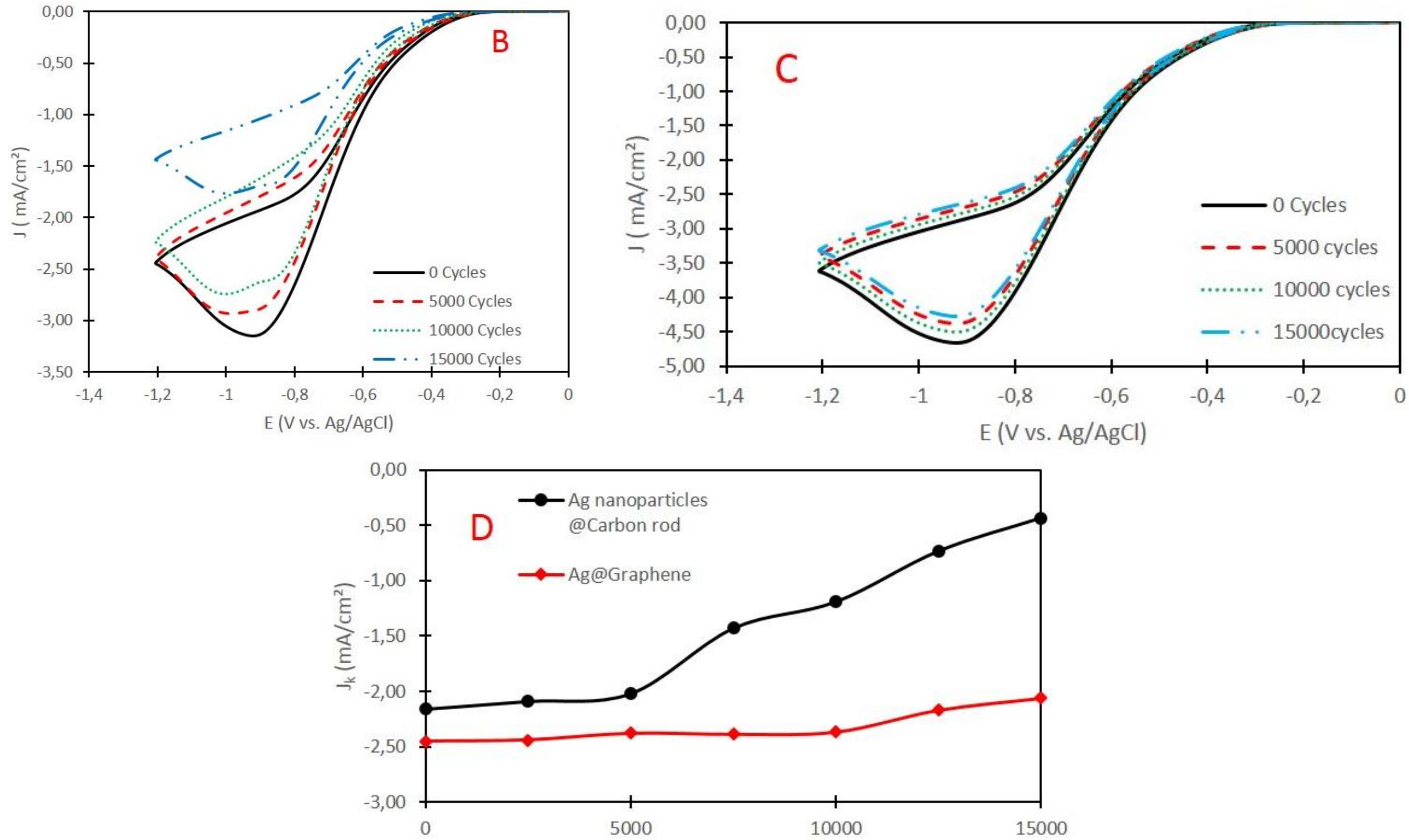


100 nm
EHT = 3.00 kV
Signal A = InLens
Mix Signal = 0.0921
Chamber = 1.80e-004 Pa
WD = 4.8 mm
Aperture Size = 20.00 µm
File Name = 170116_T3_11.tif
Date :16 Jan 2017
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0000
Chamber = 1.38e-004 Pa
WD = 4.0 mm
Aperture Size = 20.00 µm
File Name = 170117_T3_06.tif
Date :17 Jan 2017
100 nm
EHT = 15.00 kV
Signal A = InLens
Mix Signal = 0.0000
Chamber = 1.68e-004 Pa
WD = 8.4 mm
Aperture Size = 20.00 µm
File Name = 170117_T3_s139.tif
Date :17 Jan 2017
100 nm
EHT = 15.00 kV
Signal A = SE2
Mix Signal = 0.0000
Chamber = 1.68e-004 Pa
WD = 8.4 mm
Aperture Size = 20.00 µm
File Name = 170117_T3_s140.tif
Date :17 Jan 2017


100 nm
EHT = 3.00 kV
Signal A = InLens
Mix Signal = 0.0921
Chamber = 1.84e-004 Pa
WD = 4.8 mm
Aperture Size = 20.00 µm
File Name = 170116_T3_10.tif
Date :16 Jan 2017
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0000
Chamber = 1.47e-004 Pa
WD = 4.0 mm
Aperture Size = 20.00 µm
File Name = 170117_T3_04.tif
Date :17 Jan 2017
100 nm
EHT = 15.00 kV
Signal A = InLens
Mix Signal = 0.0000
Chamber = 1.72e-004 Pa
WD = 8.4 mm
Aperture Size = 20.00 µm
File Name = 170117_T3_s136.tif
Date :17 Jan 2017
100 nm
EHT = 15.00 kV
Signal A = SE2
Mix Signal = 0.0000
Chamber = 1.72e-004 Pa
WD = 8.4 mm
Aperture Size = 20.00 µm
File Name = 170117_T3_s137.tif
Date :17 Jan 2017

Univerza v Novi Gorici, Dvorec Lanthieri, 20.2.2020

After electrochemical deposition

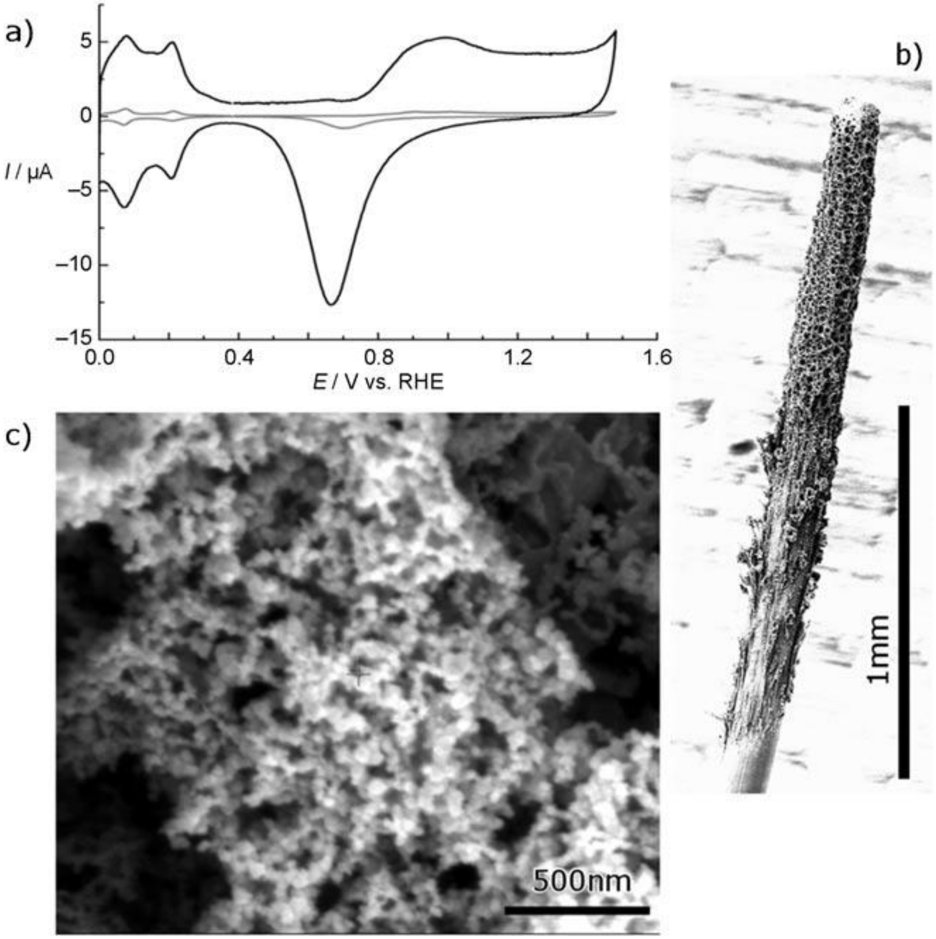


TBAP - tetrabutylammonium perchlorate + acetonitrile + benzylbromide (1 mM)

Vanrenterghrm, Chem. Comm., 2017,vol. 53, pp.9340-9343.

There is something else occurring at negative potentials!

Cathodic Corrosion: A Quick, Clean, and Versatile Method for the Synthesis of Metallic Nanoparticles



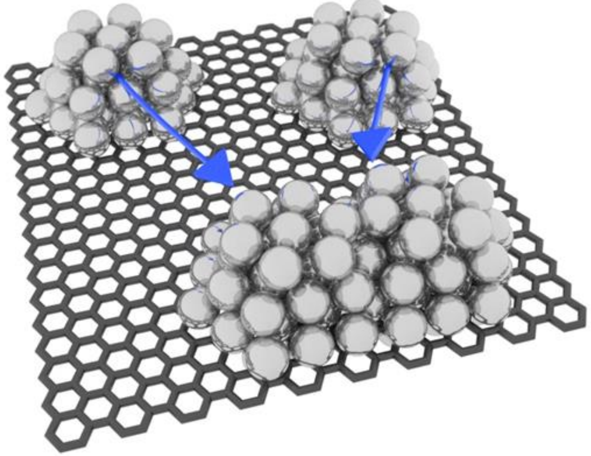
Cyclic voltammogram of a Pt wire 135 mm in diameter, submerged by 1 mm in 0.5m H2SO4 before (gray) and after (black) the wire was held for 1000 s at a dc of 10 V (7.2 V vs. HgO) in 10m NaOH. Graphite is used as anode to rule out the formation of interfering species by anodic dissolution. Sweep rate: 50 mVs1. b,c) Typical scanning electron microscopic images of a well-rinsed Pt electrode after cathodic treatment.

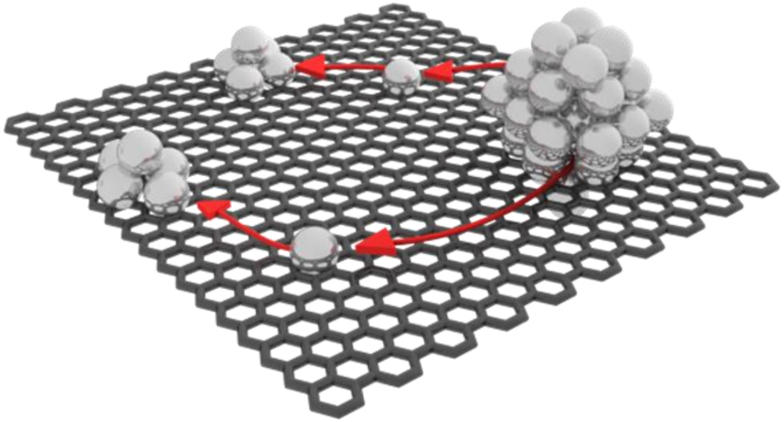
Angew. Chem. Int. Ed. 2011, 50, 6346 –6350

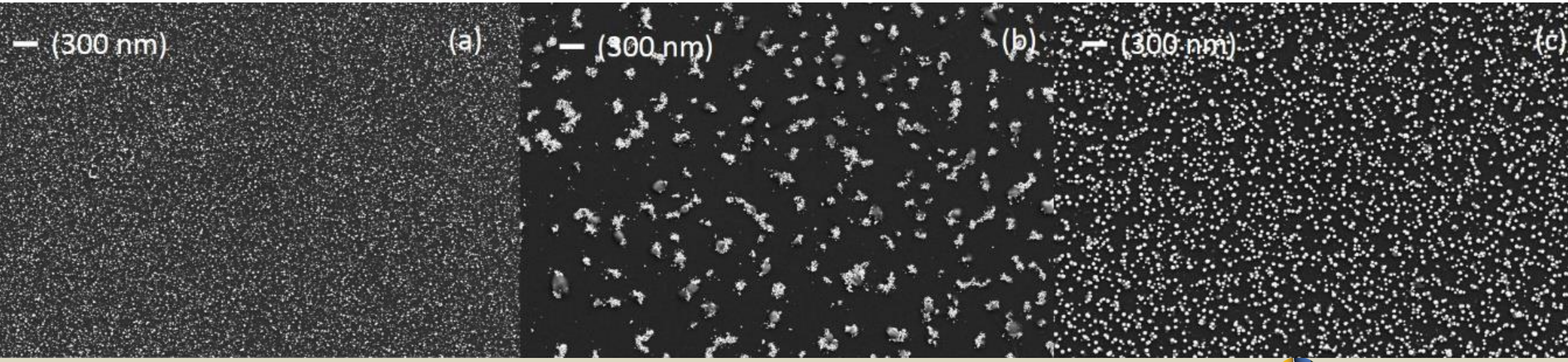
What about degradation at reductive potentials?

Electrochemical induced metal nanoparticle Coalescence / Dispersion

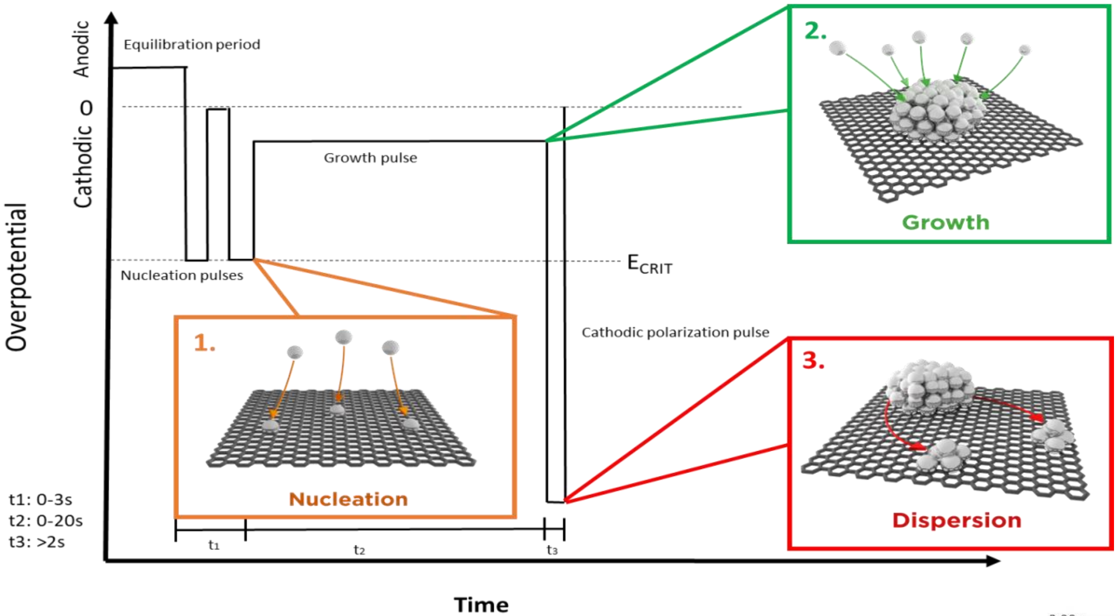
Interplay between Potential induced Agglomeration vs. Dispersion

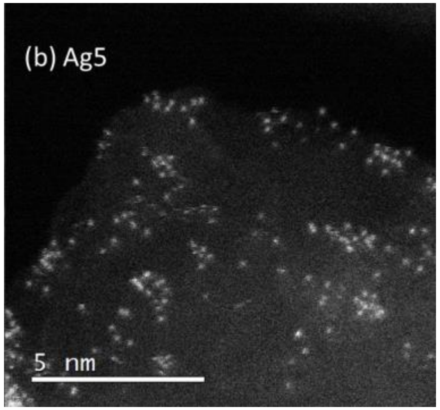


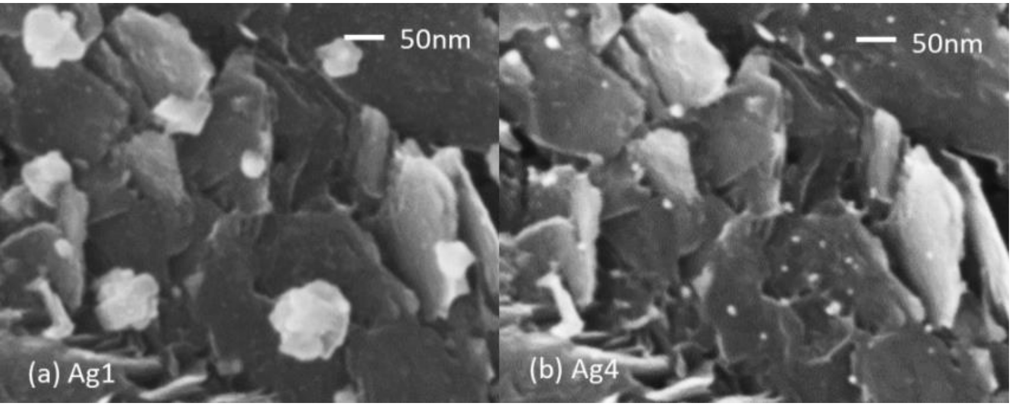


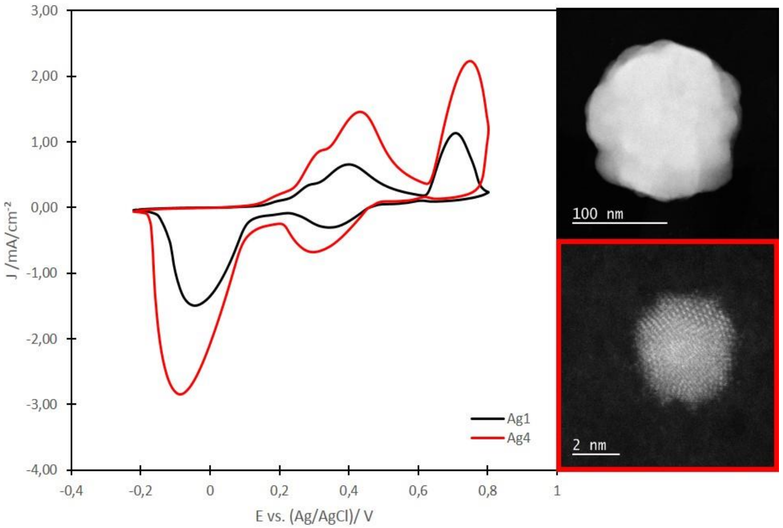


Vanrenterghrm, Applied Catalysis B: Environmental, 2018, 226, pp 396–402.





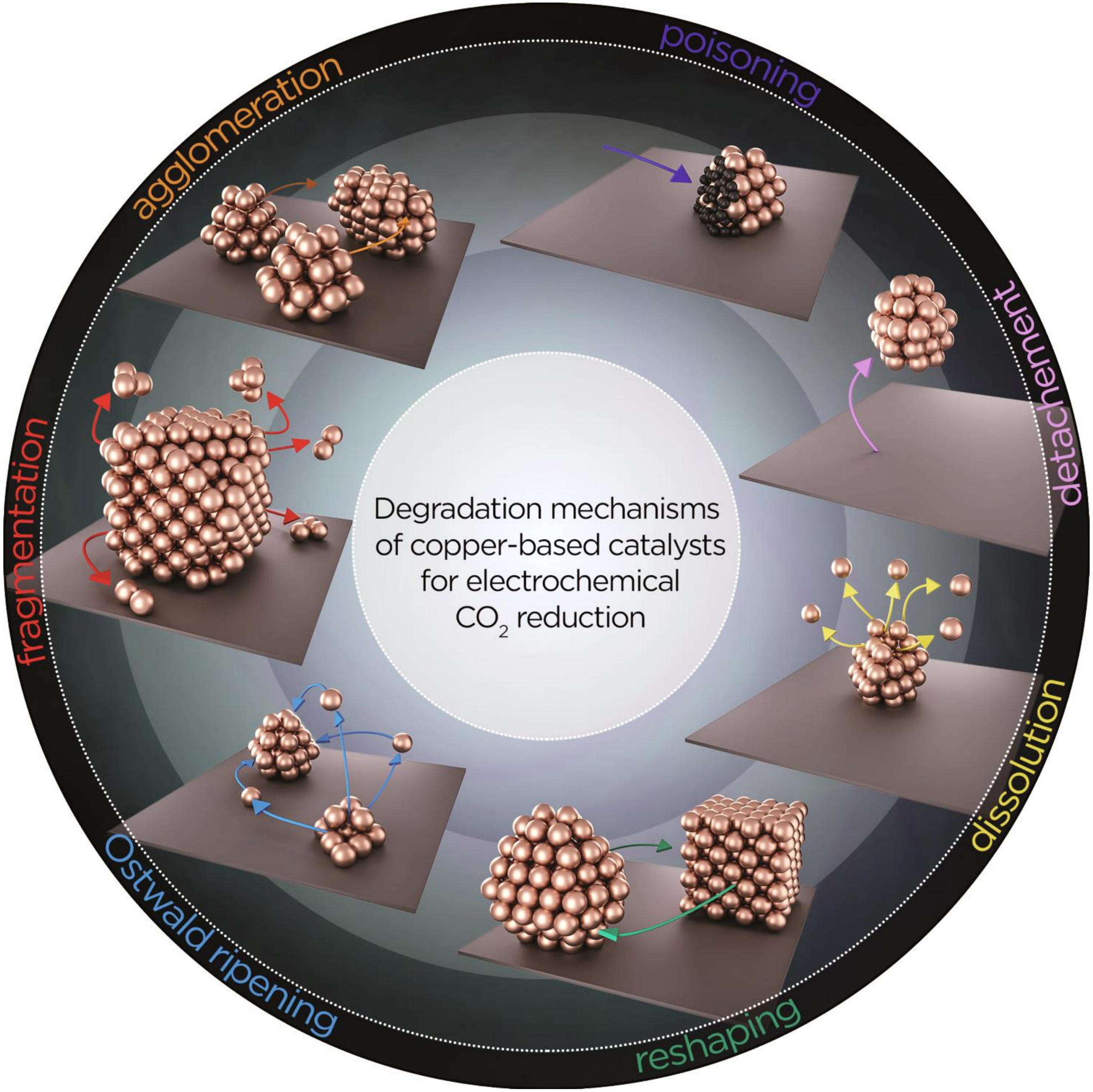




TBAP - tetrabutylammonium perchlorate + MeOH, acetonitrile and dimethylsulfoxide

Also Pt, Ni, Au and Pd

Vanrenterghrm, Applied Catalysis B: Environmental, 2018, 226, pp 396–402.



Degradation mechanisms of copper-based catalysts for electrochemical CO_2 reduction
poisoning
detachement
dissolution
reshaping
Ostwald ripening
fragmentation
agglomeration

Univerza v Novi Gorici, Dvorec Lanthieri, 20.2.2020

arrs
JAVNA AGENCIJA ZA RAZISKOVALNO DEJAVNOST REPUBLIKE SLOVENIJE

Thanks to ARRS for MR, for postdoc project, for money to visit ERC holder, for complementary scheme, for bilateral projects, itd.!

JAVNI SKLAD REPUBLIKE SLOVENIJE ZA RAZVOJ KADROV IN ŠTIPENDIJE AD FUTURA

Thanks to Ad futuri visiting scholarship to go abrad!

MARIE CURIE ACTIONS

Thanks Marie Skłodowska-Curie actions Individual Fellowships!

Thanks to all my mentors and the awesome team for supporting and improving me!

Thanks erc!

Thank you for your attention!

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

What is stabiltiy?

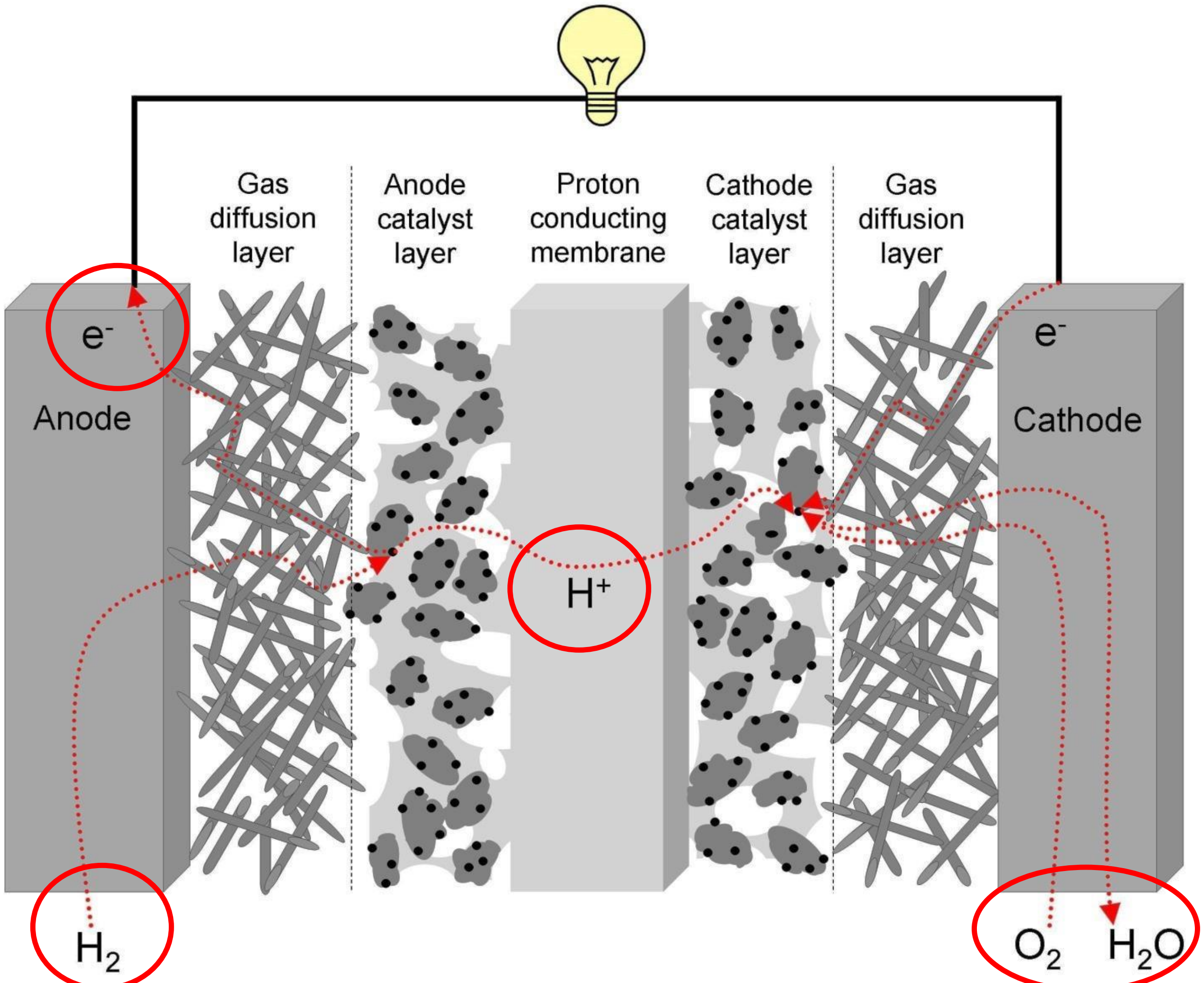
- Changing the structure of the catalyst over time
  - thereby affecting its activity
- Precious metals as raw materials are rare, expensive and unevenly distributed (critical)
- At the same time, understanding is also very important for the purpose of recycling these metals

2020 Summer Olympics Japan

"Tokyo 2020 medals will be made from electronic waste, or urban e-waste, containing significant amounts of gold, silver and copper."

Big environmental problem in developing countries!

PEM-FC – what do we need?



On macroscale: gas diffusion electrodes

http://www.pfrang.de/pageID_2388563.html