Nanoscale behaveour and properties of noble metals in electrochemical environment

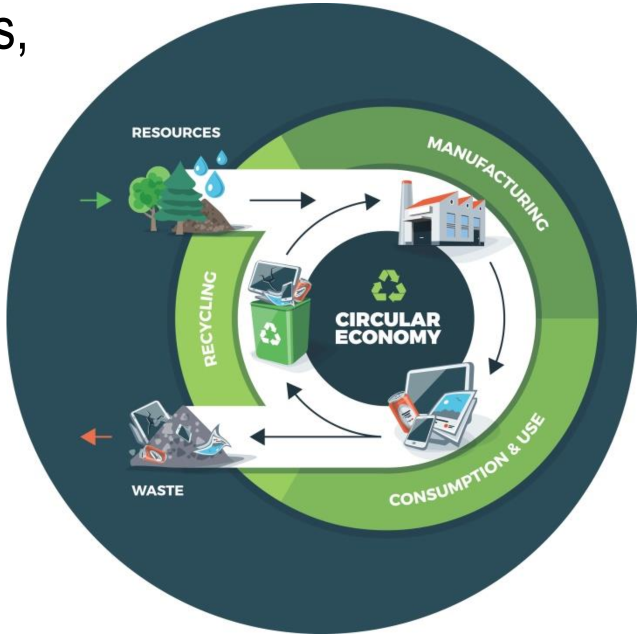
NATIONAL INSTITUTE OF CHEMISTRY

D13 Department of Catalysis and Chemical Reaction Engineering
Dr. Nejc Hodnik
in close colaboration with D10 and D04

On one side our development and life quality is dependent on raw materials resources and economics, however on the other side it is limited by pollution and negative climate changes.

Strategies towards sustainable future:

- EU's transition to a **circular economy**
  - no supply risk!
- EU's transition to a **low-carbon economy**
  - clean and renewable energy!



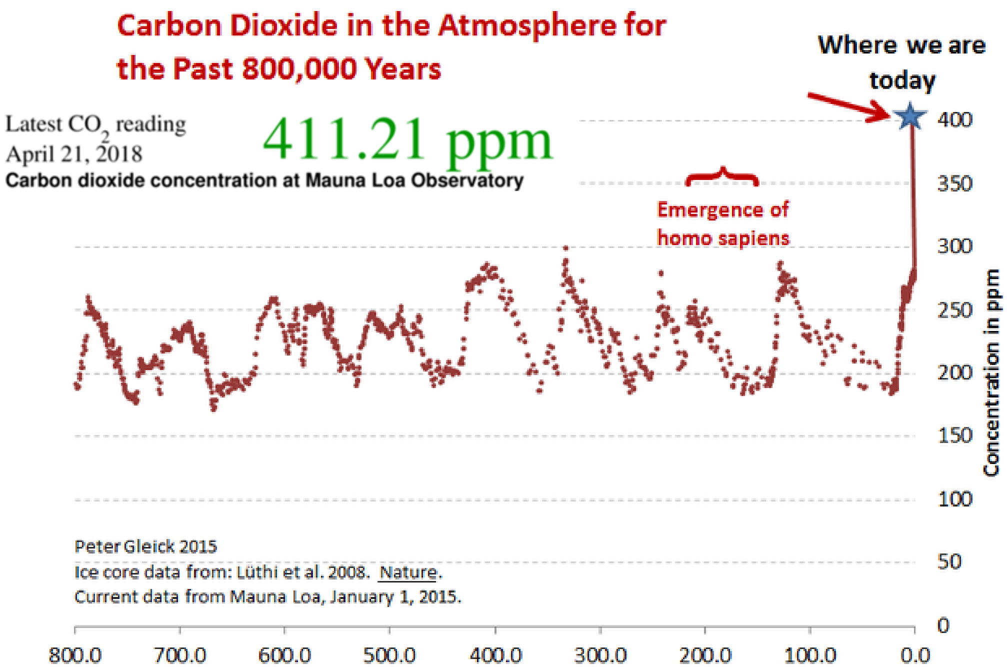
http://www.ies.be/node/3632

http://www.ft.lk/article/482633/Green-finance--Financing-the-transition-towards-a-low-carbon-economy

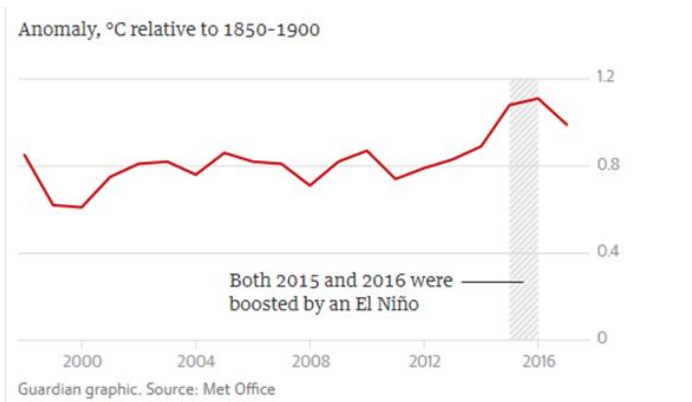
Problem! Global Warming!

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



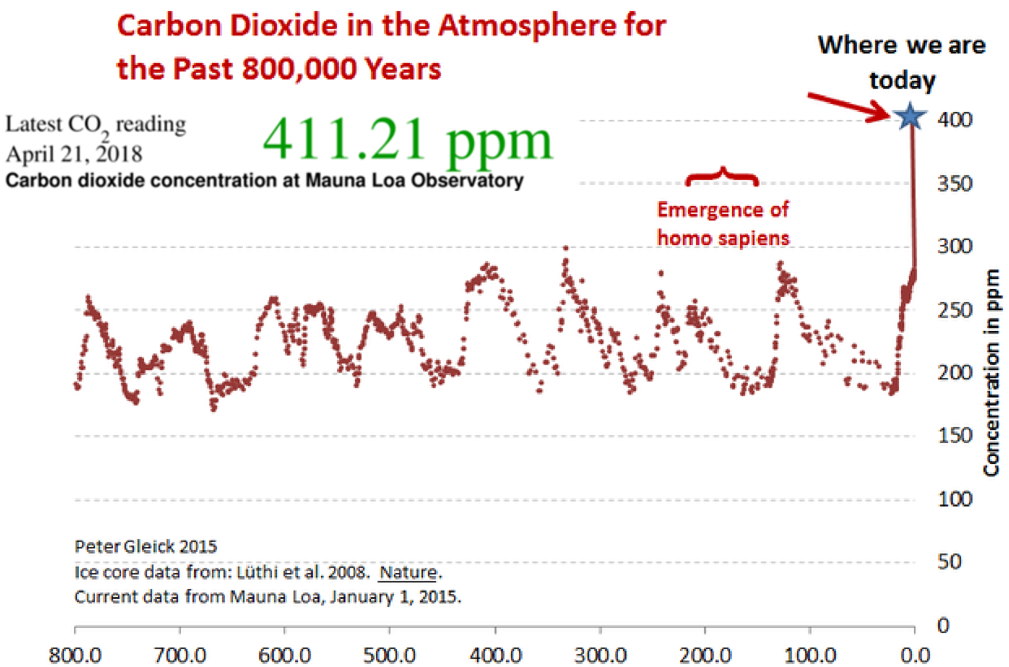
https://scripps.ucsd.edu/programs/keelingcurve/

-2016 was the warmest in history
-17 out of 18 warmest years were after 2001

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“

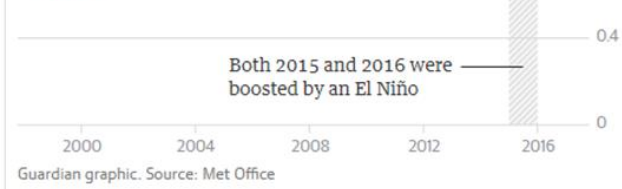


https://scripps.ucsd.edu/programs/keelingcurve/

-2016 was the warmest in history
-17 out of 18 warmest years were after 2001

Pollution

-> to lower atmospheric pollution levels in big cities



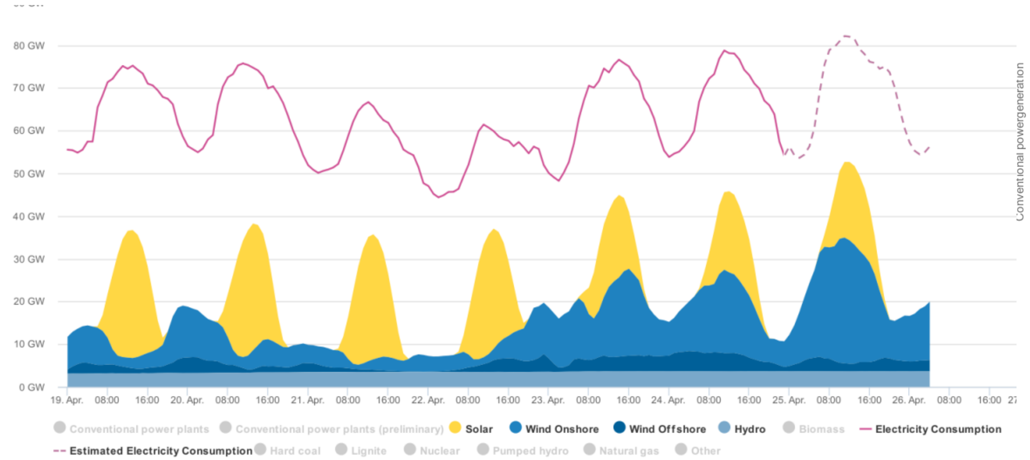
http://www3.epa.gov/climatechange/ghgemissions/global.html

NEJC HODNIK

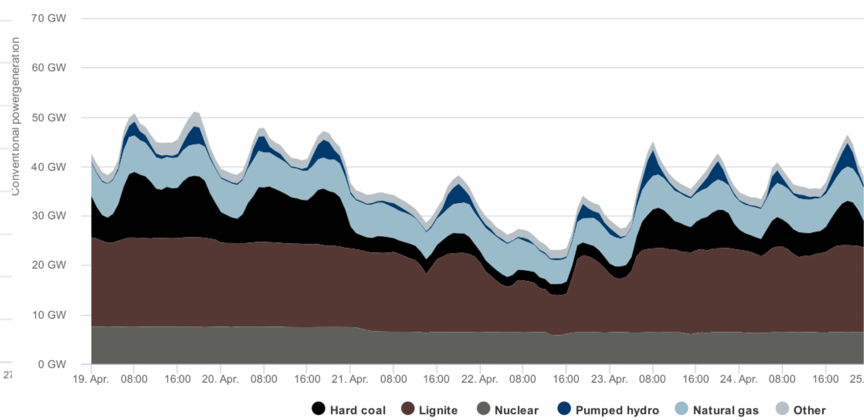
Forum40, Maj 2018, Ljubljana

What we can do?

- As scientists we can find new or more efficient ways for everyday tasks to be (more) sustainable.
- To lower the dependance from fossile fuels
  - Like turning CO_2 to chemicals or biomass to fuel
- **Utilize intermittent energy sources like sun and wind (renewable sources)**
- **Current Grand Challenges: to store energy & catalytic conversion processes**



The fluctuating Germany energy production from wind and solar including (mismatched) power demand in the last week.



Conventional Power Generation

https://www.agora-energiewende.de/en/topics/-agothem-/Produkt/produkt/76/Agorameter/

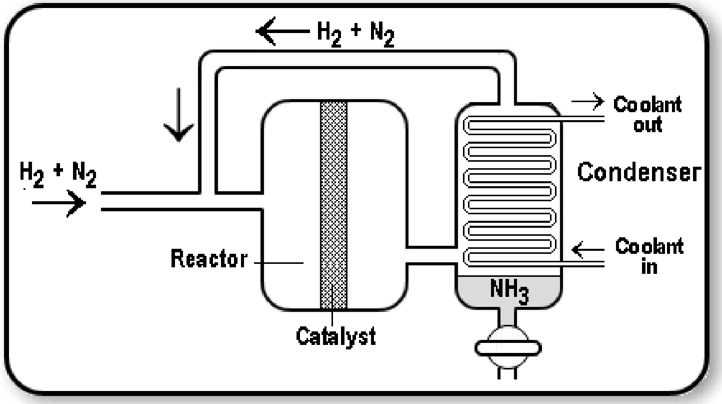
What we can do?

- Example from history: **Haber–Bosch process** (1910)**:**
- is an artificial nitrogen fixation 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

- Although the Haber process is mainly used to produce fertilizer today, during World War I it provided Germany with a source of ammonia for the production of explosives.



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

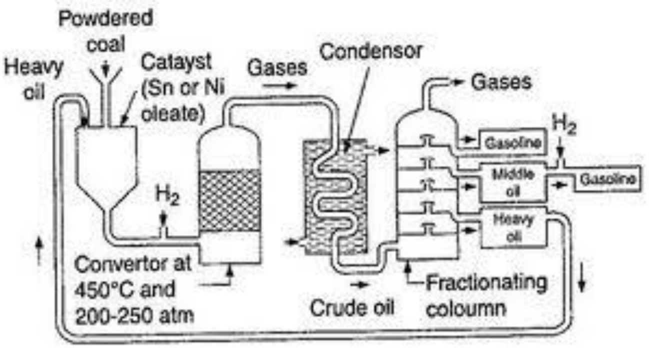
What we can do?

- 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.
- 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 a collection of chemical reactions that converts a mixture of **carbon monoxide** (**CO**) and **hydrogen** (**H_2**) **into liquid hydrocarbons - fuel**.



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

What we can do?

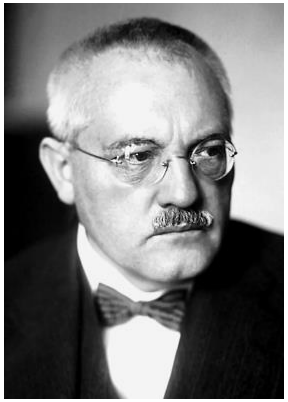
- Example from history: **Bergius process** (1913):
- is a method of production of **liquid synthetic fuel** by catalytic hydrogenation of high-volatile bituminous coal at high temperature and pressure.
- Before the Bergius process, liquid fuel like diesel oil or petrolium was difficult to get, especially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

Fredrich Bergius
1931 - Nobel Prize

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

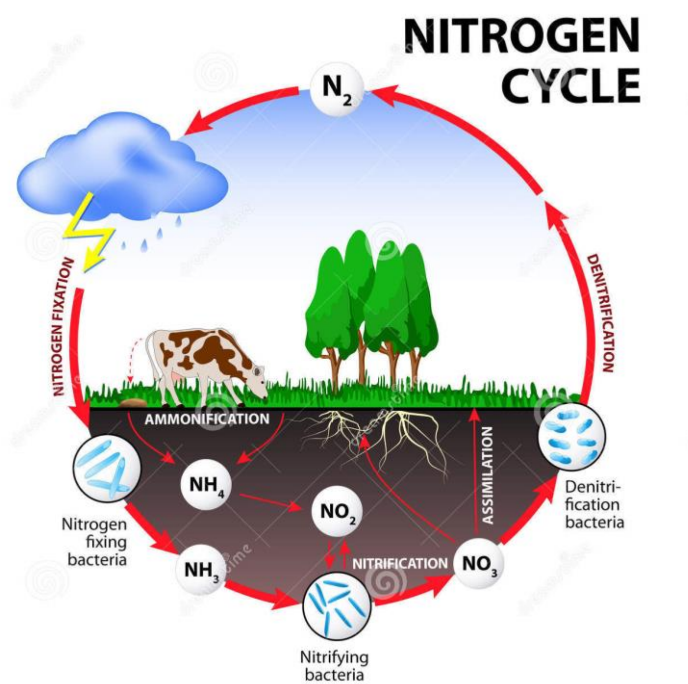
- The Fischer–Tropsch process (1925) is a collection of chemical reactions that converts a mixture of **carbon monoxide** (**CO**) and **hydrogen** (H_2) **into liquid hydrocarbons - fuel**.

Carl Bosch
1931 - Nobel Prize

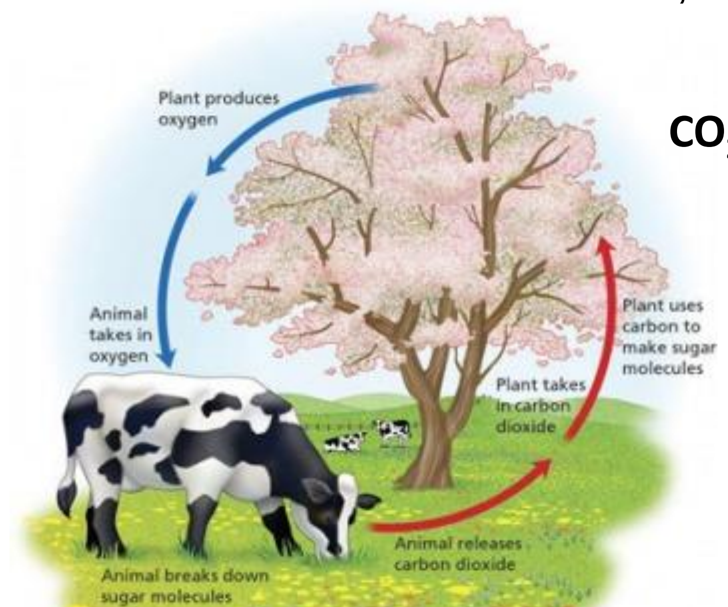


NEJC HODNIK

Forum40, Maj 2018, Ljubljana



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

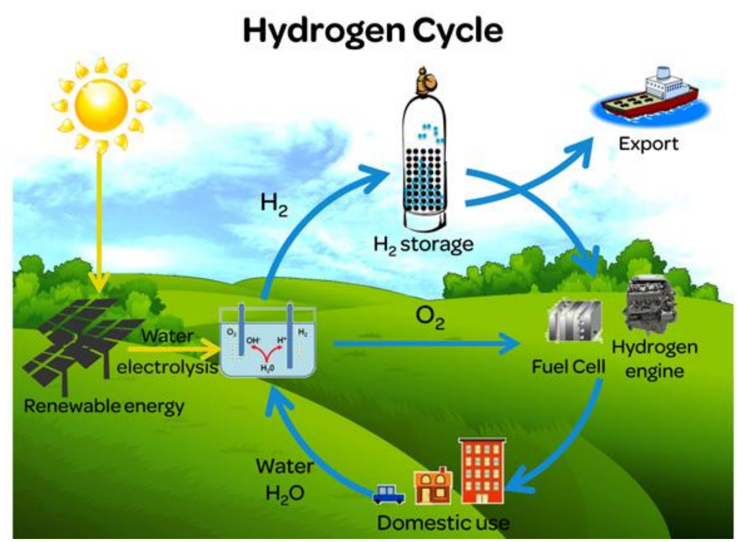


CO_2 cycle

Energy

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

Fertilizer -> food



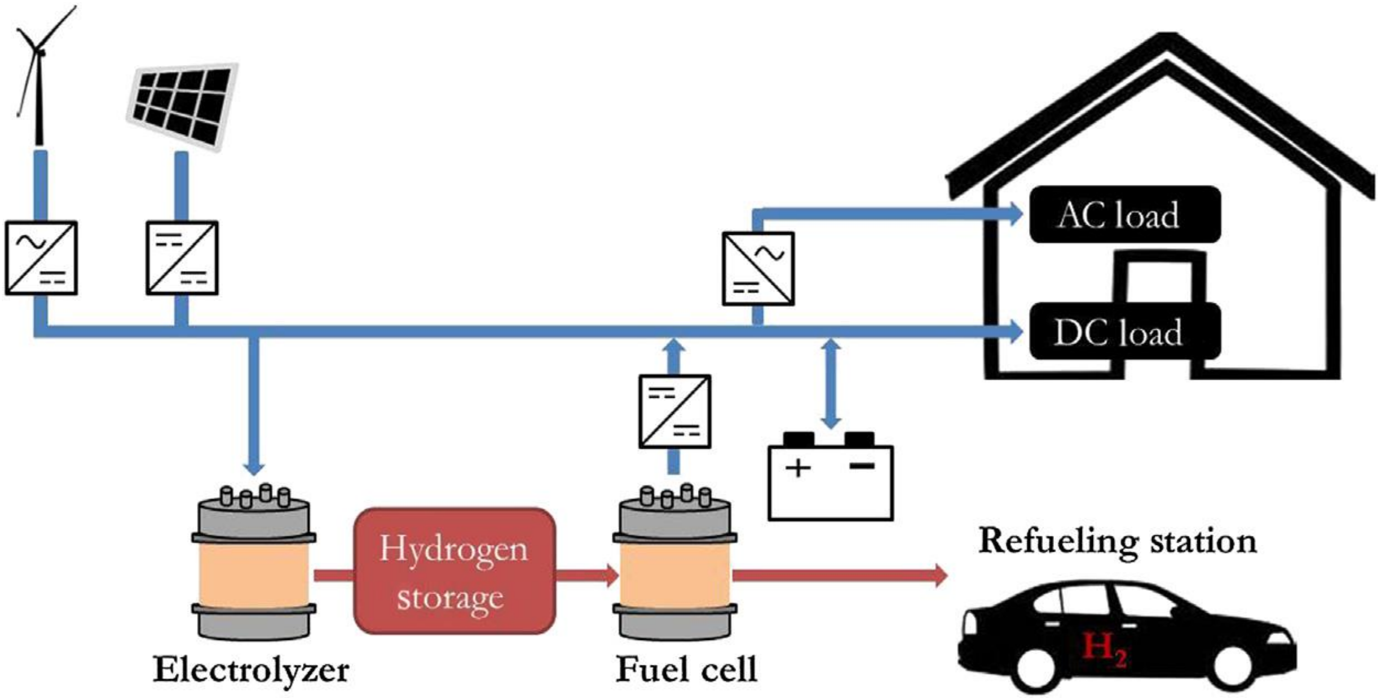
Common for all conversion processes -> catalysis

-90-95% of all industrial chemical processes

http://www.merlin.unsw.edu.au/energyh/about-hydrogen-energy/

What we can do?

- **Hydrogen cycle at home:**
- self sustained hydrogen home

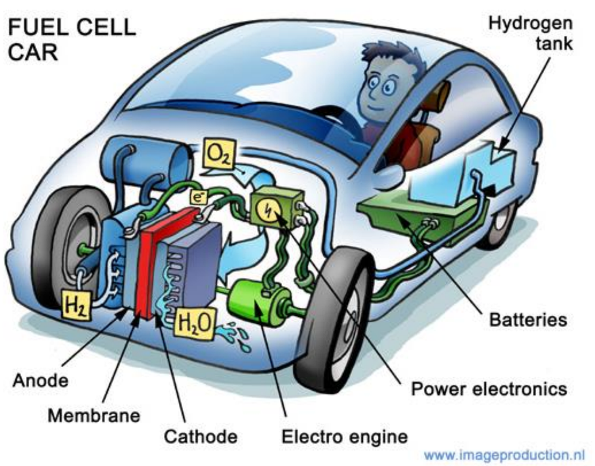


Current Grand Challenges: to store energy & better catalytic processes

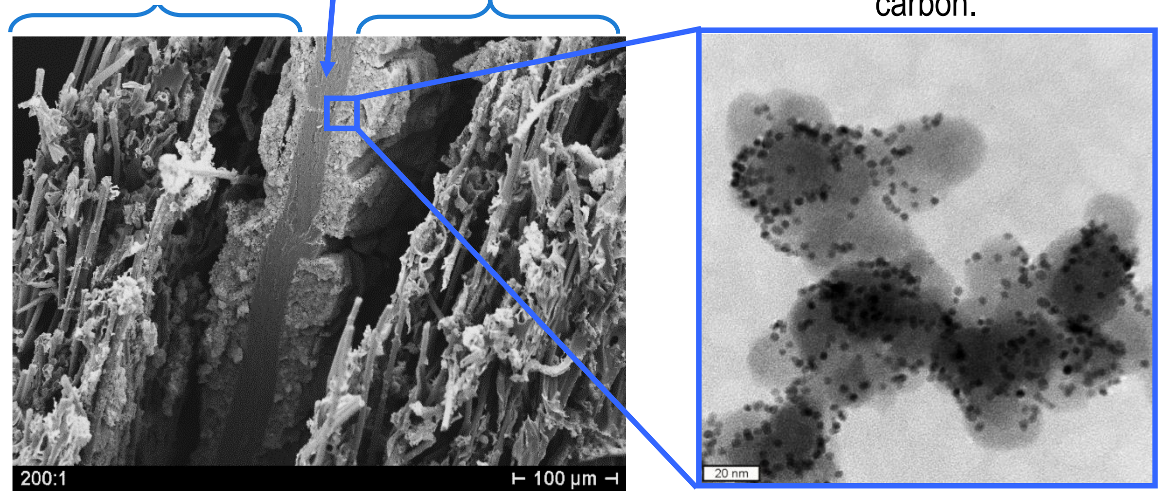
NEJC HODNIK

Proton exchange membrane fuel cell

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



Anode Membrane Cathode

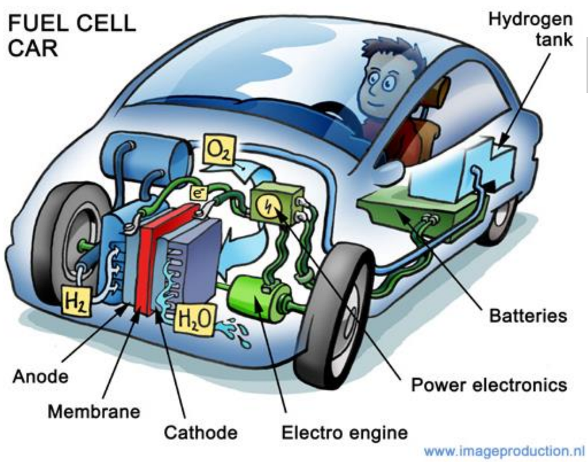


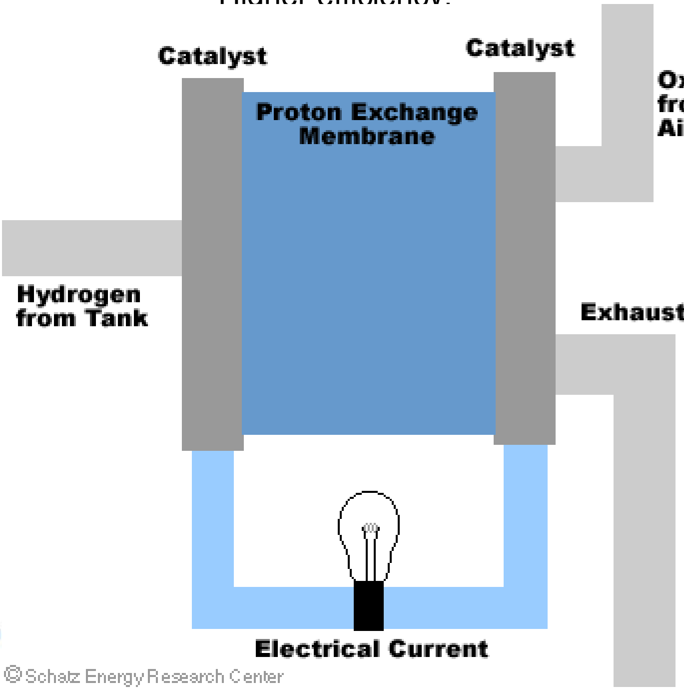
Electrocatalysts are Pt-based nanoparticles on high surface carbon.

Proton exchange membrane fuel cell

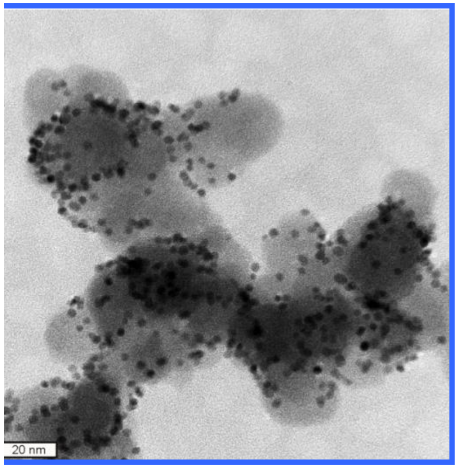
No emissions – no CO_2! Only $2H_2 + O_2 \rightarrow 2H_2O$

Higher efficiency!





Electrocatalysts are Pt-based nanoparticles on high surface carbon.

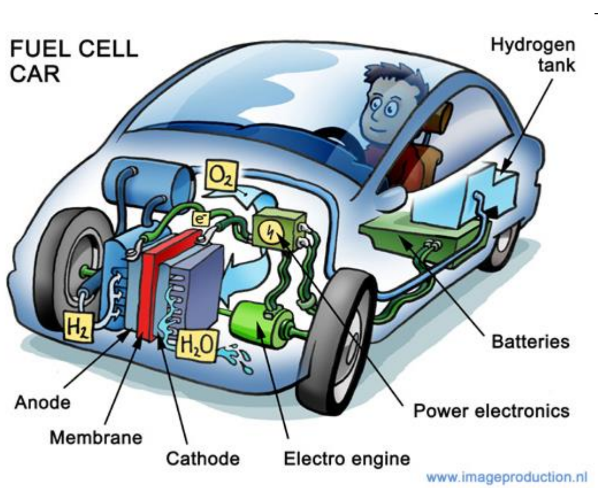


NEJC HODNIK

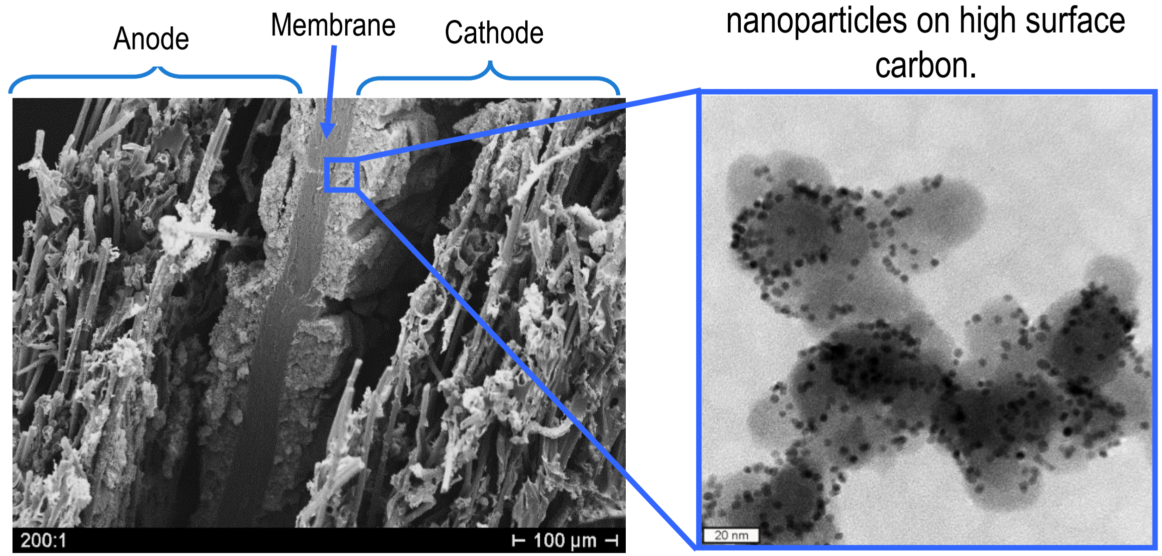
Forum40, Maj 2018, Ljubljana

Proton exchange membrane fuel cell

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



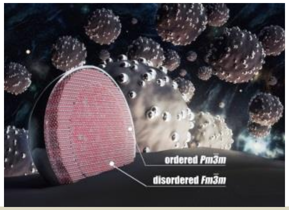
Electrocatalysts are Pt-based nanoparticles on high surface carbon.



PEM-FC electrocatalyst stil requires improvement of performance & stability & cost !

Most promising replacement of Pt/C are Pt-alloys, at least activity wise – therefore it is important to study their electrochemical behaveour – their stability!

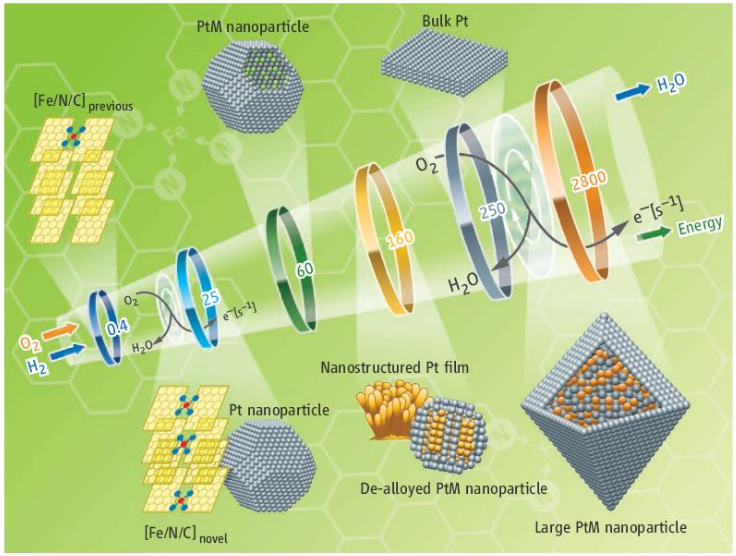
$PtCu_3$ nanoparticles...
- US 9147885 **Patent**



Proton exchange membrane fuel cell

- What defines metal electrocatalyst perfomance:
  - double layer structure (what defines that…)

Gasteiger & Markovic
SCIENCE VOL 324 3 APRIL 2009



-nature of the metal
-surface facets (morphology)
-presence of defects, steps, kinks, ad-atoms (structure)
-presence of second metal (composition&structure)
-size
-support
-electrolyte (double layer)

Practically everything we can think of!

ligand and/or strain, morphology, confinement effect, surface segregation, proximity, ensemble, surface patterning, size, etc., effect

NEJC HODNIK

Proton exchange membrane fuel cell

- What defines metal electrocatalyst perfomance:
  - double layer structure (what defines that…)

Gasteiger & Markovic

-nature of the metal
-surface facets (morphology)
-presence of defects, steps, kinks, ad-atoms (structure)
-presence of second metal (composition&structure)
-size
-support
-electrolyte (double layer)

Practically everything we can think of!

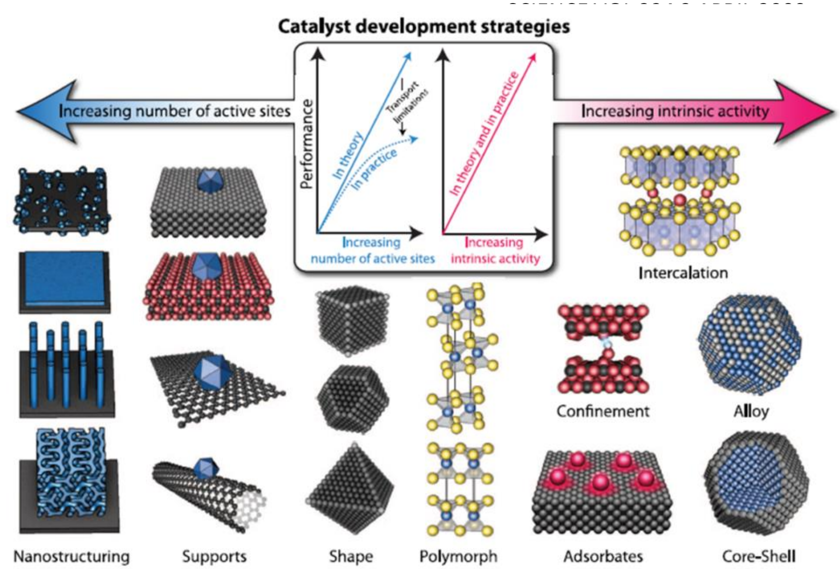
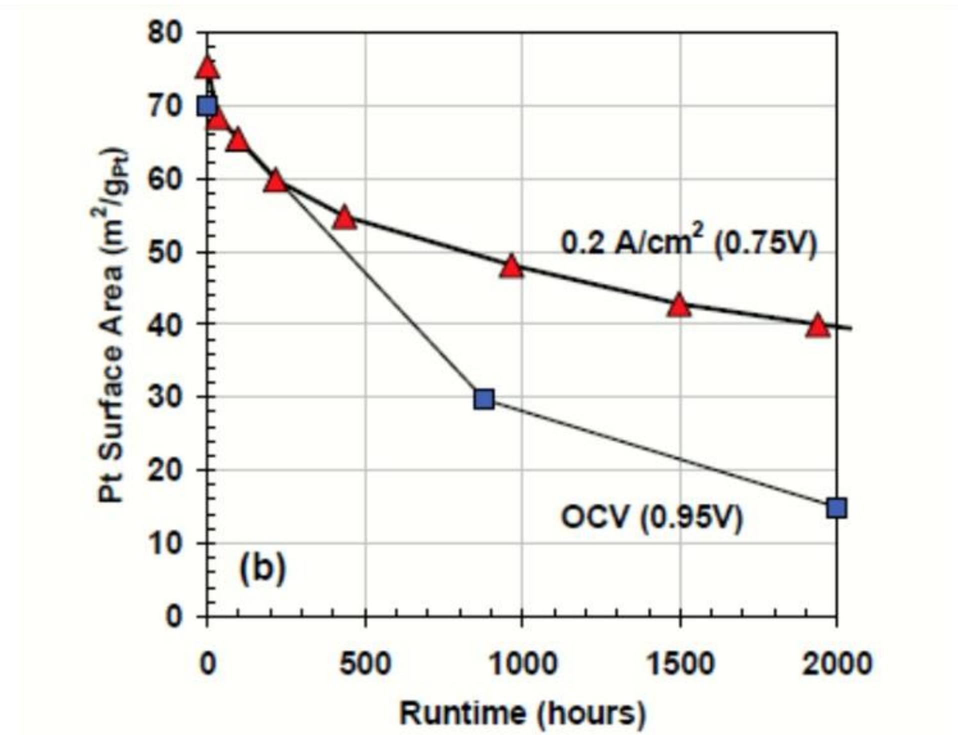
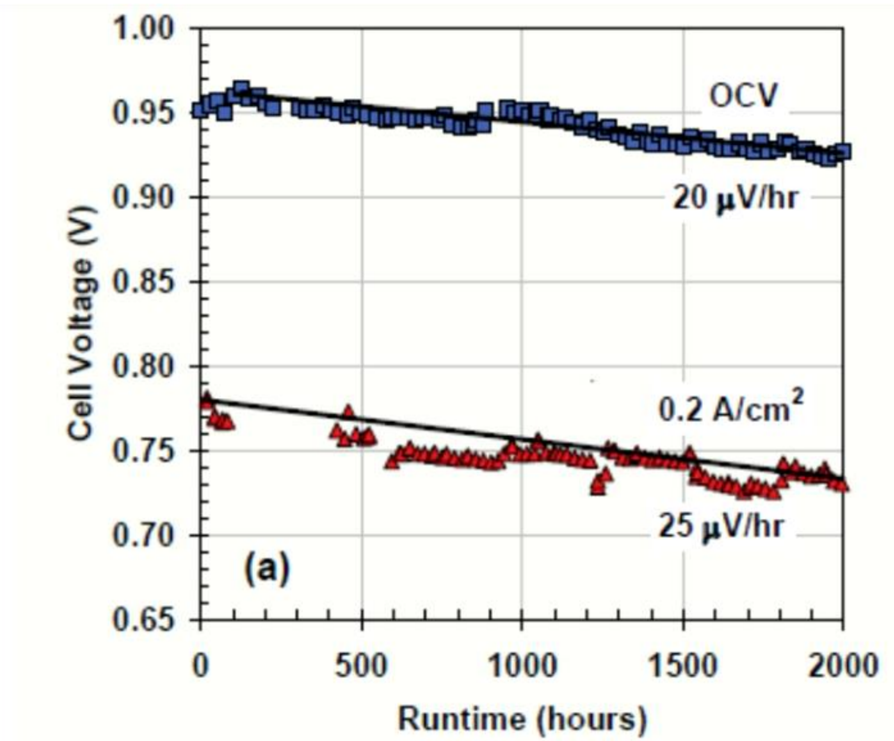


Fig. 2. Catalyst development strategies. Schematic of various catalyst development strategies, which aim to increase the number of active sites and/or increase the intrinsic activity of each active site.

ligand and/or strain, morphology, confinement effect, surface segregation, proximity, ensemble, surface patterning, size, etc., effect

Proton exchange membrane fuel cell

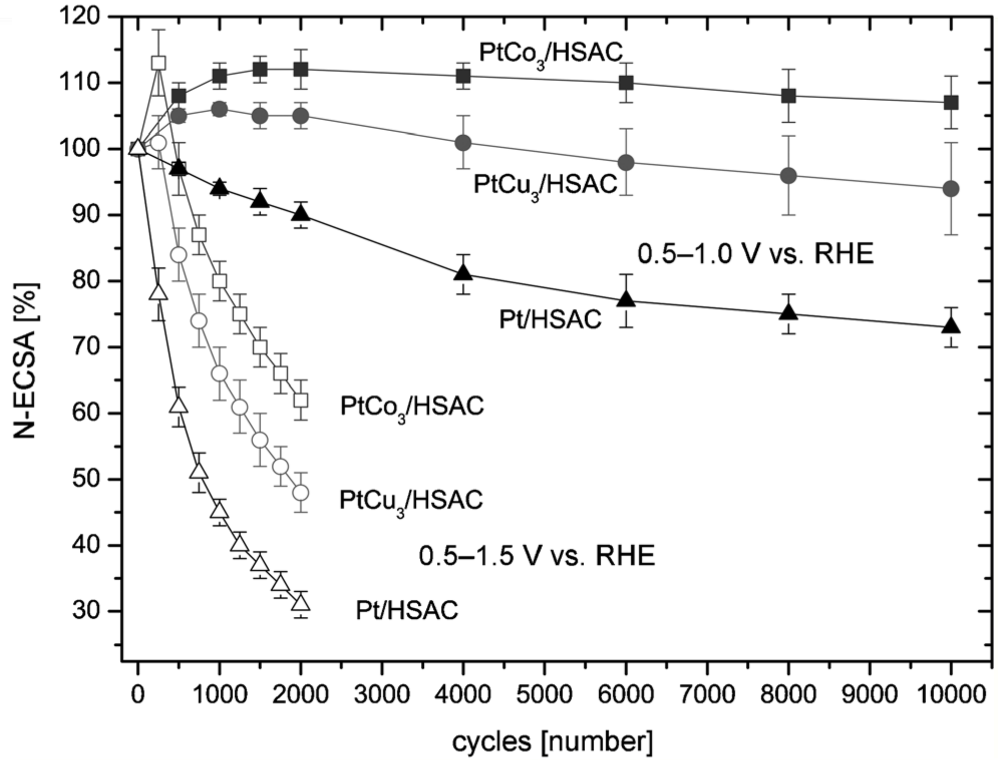




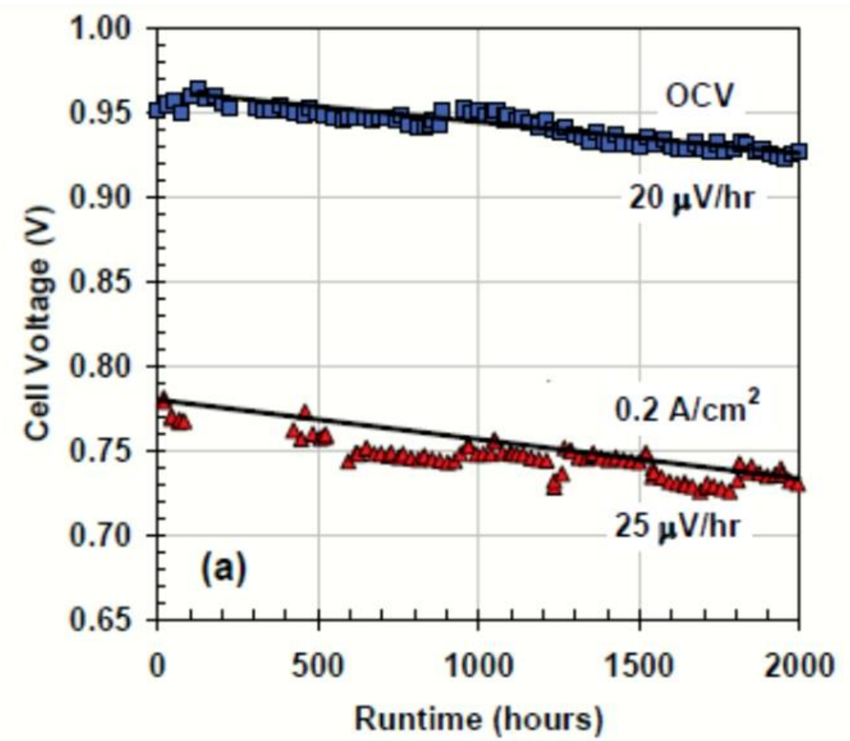
Is it possible to avoid this – we must truly understand fundamentals first –> ex-situ tests

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

Proton exchange membrane fuel cell



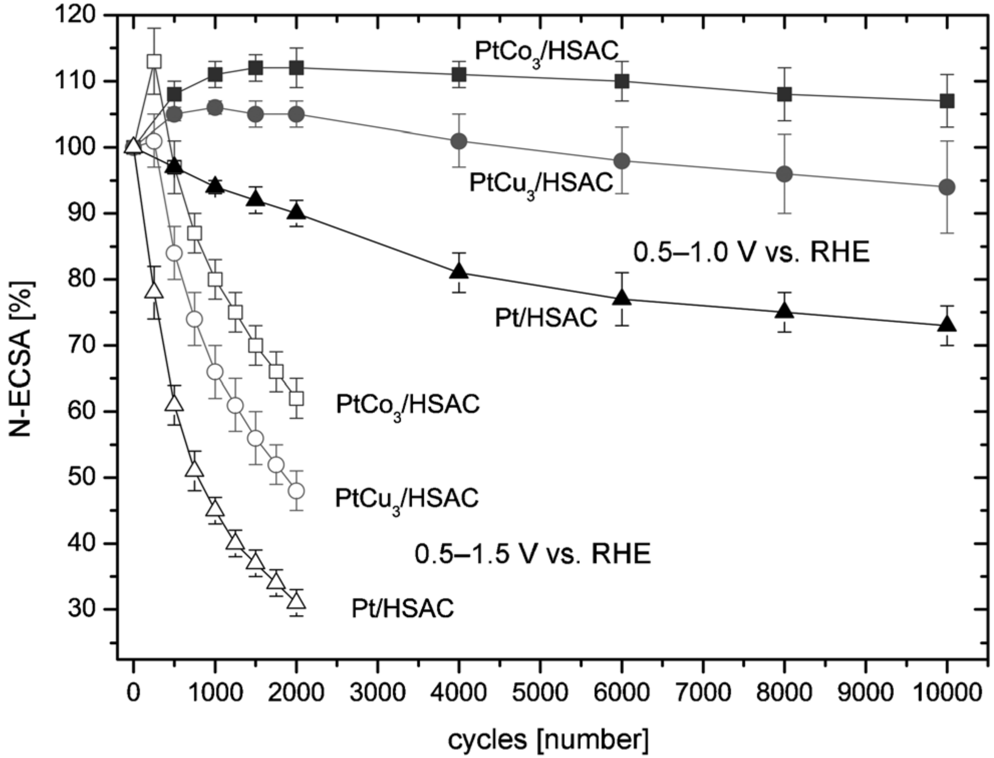
Frédéric Hasché, Activity, *ChemCatChem*, 3, (2011) 1805



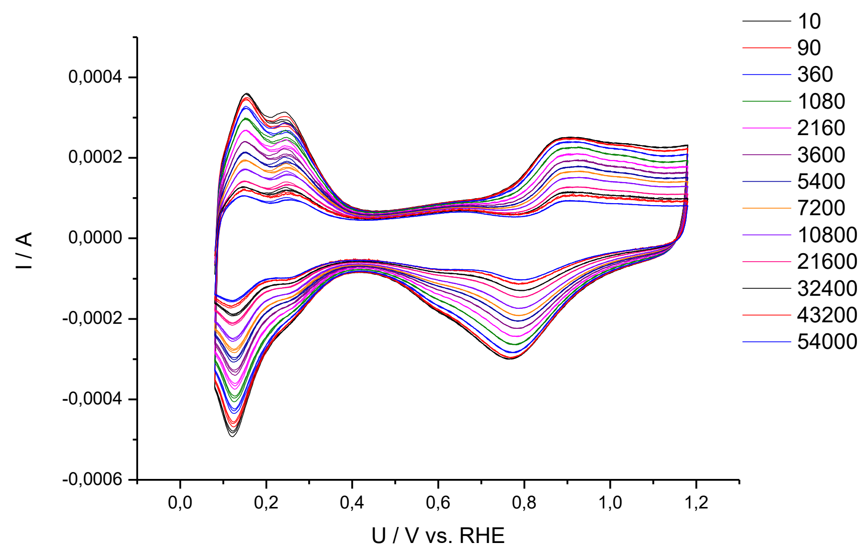
Is it possible to avoid this – we must truly understand fundamentals first –> ex-situ tests

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

Proton exchange membrane fuel cell



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

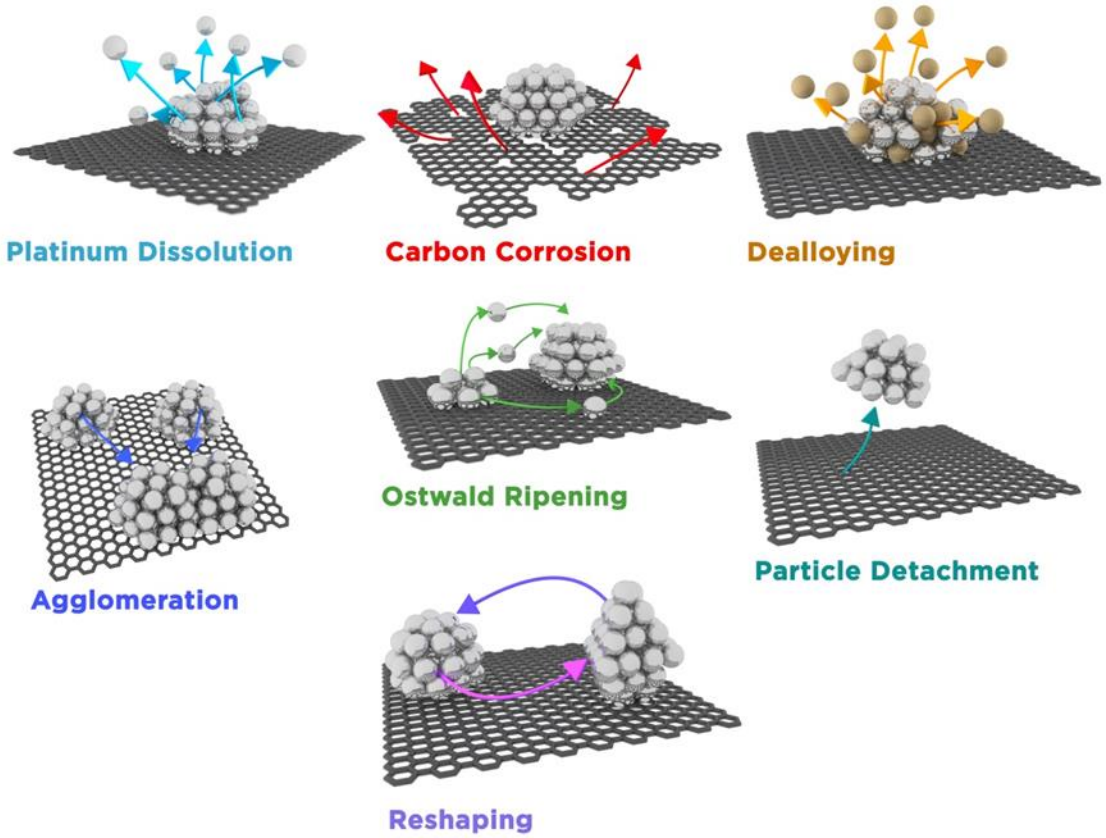


Is it possible to avoid this – we must truly understand fundamentals first –> ex-situ tests

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

• Topic 2: **Degradation studies**

Mechanisms for the loss of active surface area:



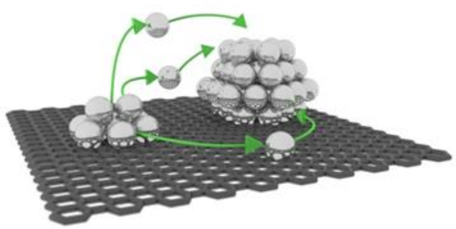
Most studies performed on Pt or PGM at low pH – Fuel Cell.

Degradation at oxidative potentials!

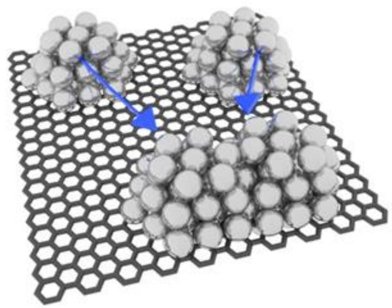
Hodnik, et al; *Acc. Chem. Res.*, **2016**, 49 (9), pp 2015–2022

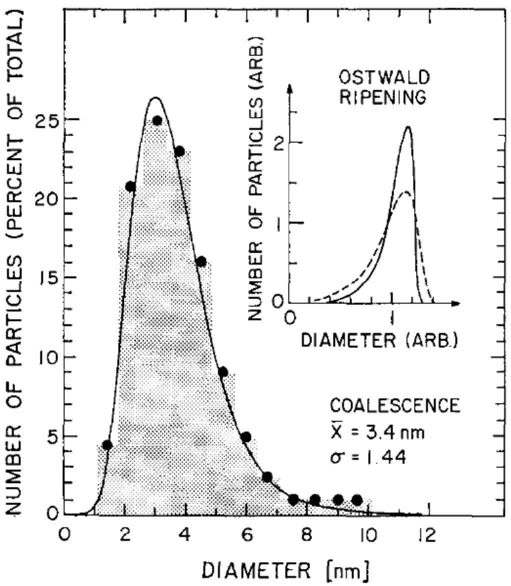
How to distinguish between them?

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**.





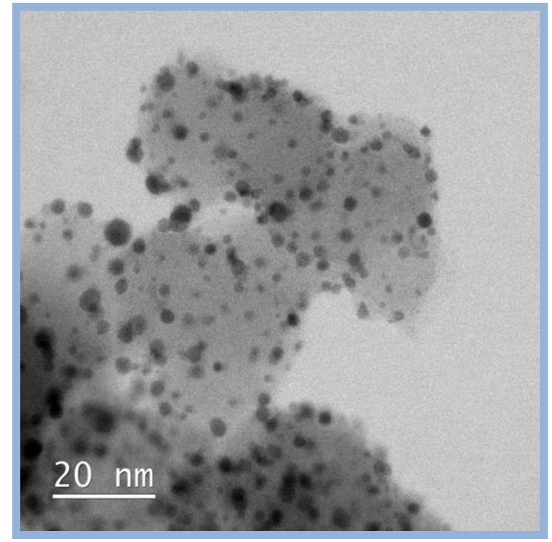
Problem: the simple models assume that only one growth mode occurs! – not true!

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

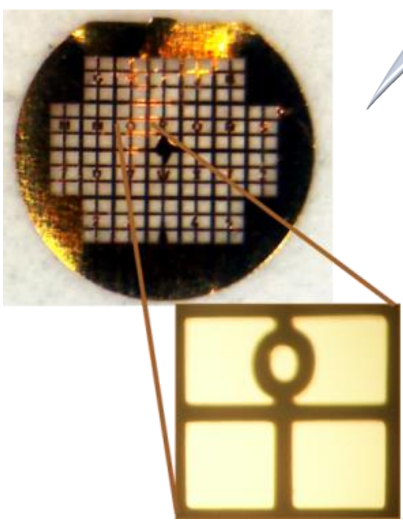
C.G. Granqvist, R.A. Buhrman, Journal of Catalysis , **1976**, 42, 477-479.

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



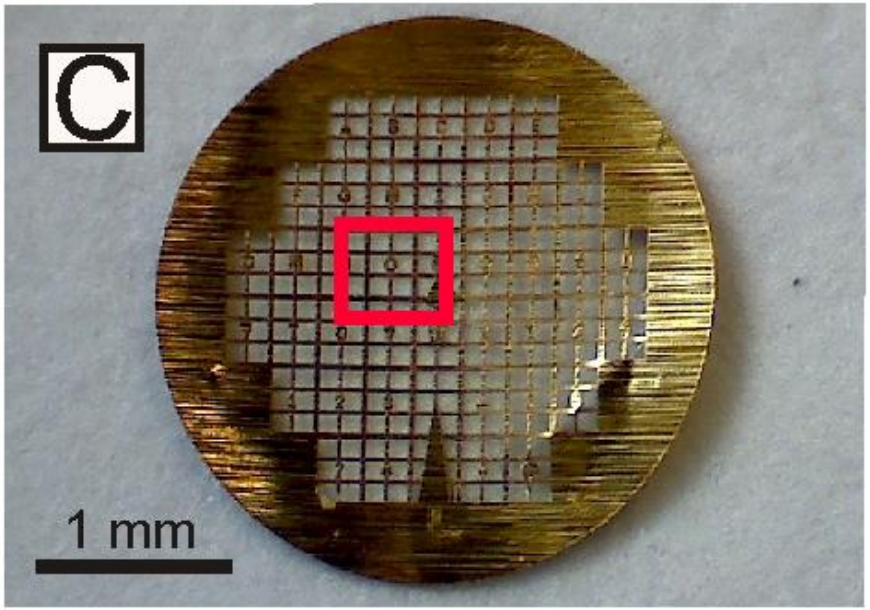
The Gold finder TEM grid allows to retrieve the same spot throughout the electrochemical treatments.

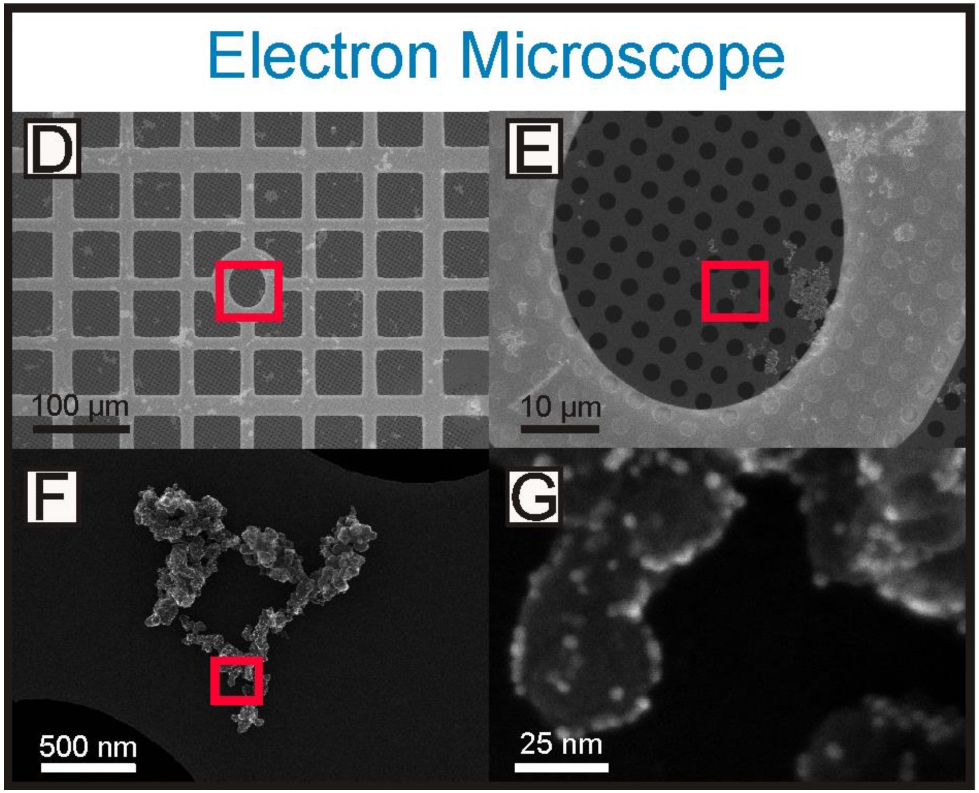


Atomic resolution STEM - JEOL ARM 200 CF

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.



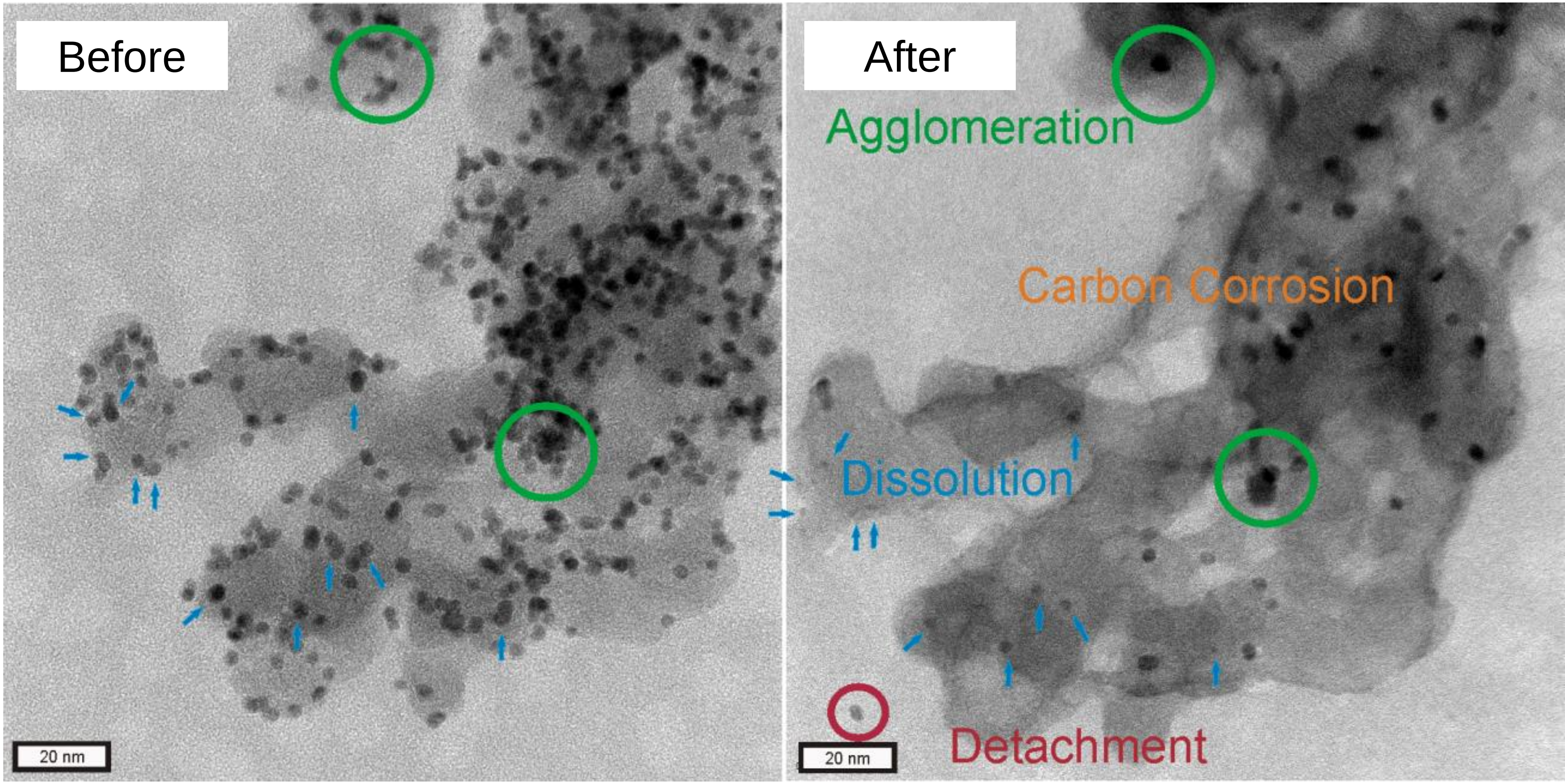


- Utilizing a TEM finder grid as a WE
  - Conducting, but inert Au

- Tracking of the catalyst particles
  - Alphanumerical signs for orientation

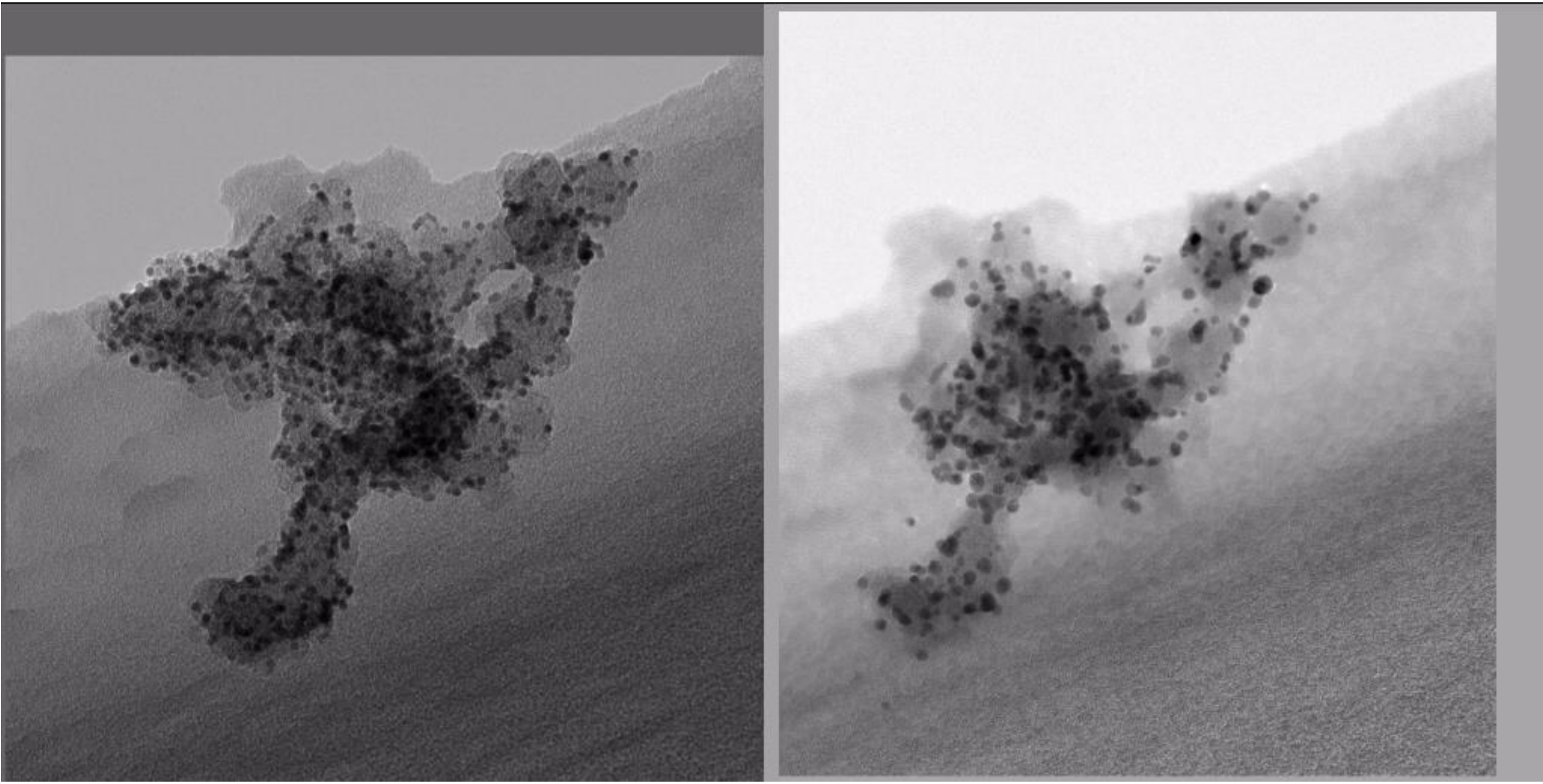
Pt/Vulcan
(20 wt.%, 3.6 nm)

Overlapping degradation mechanisms – material dependant



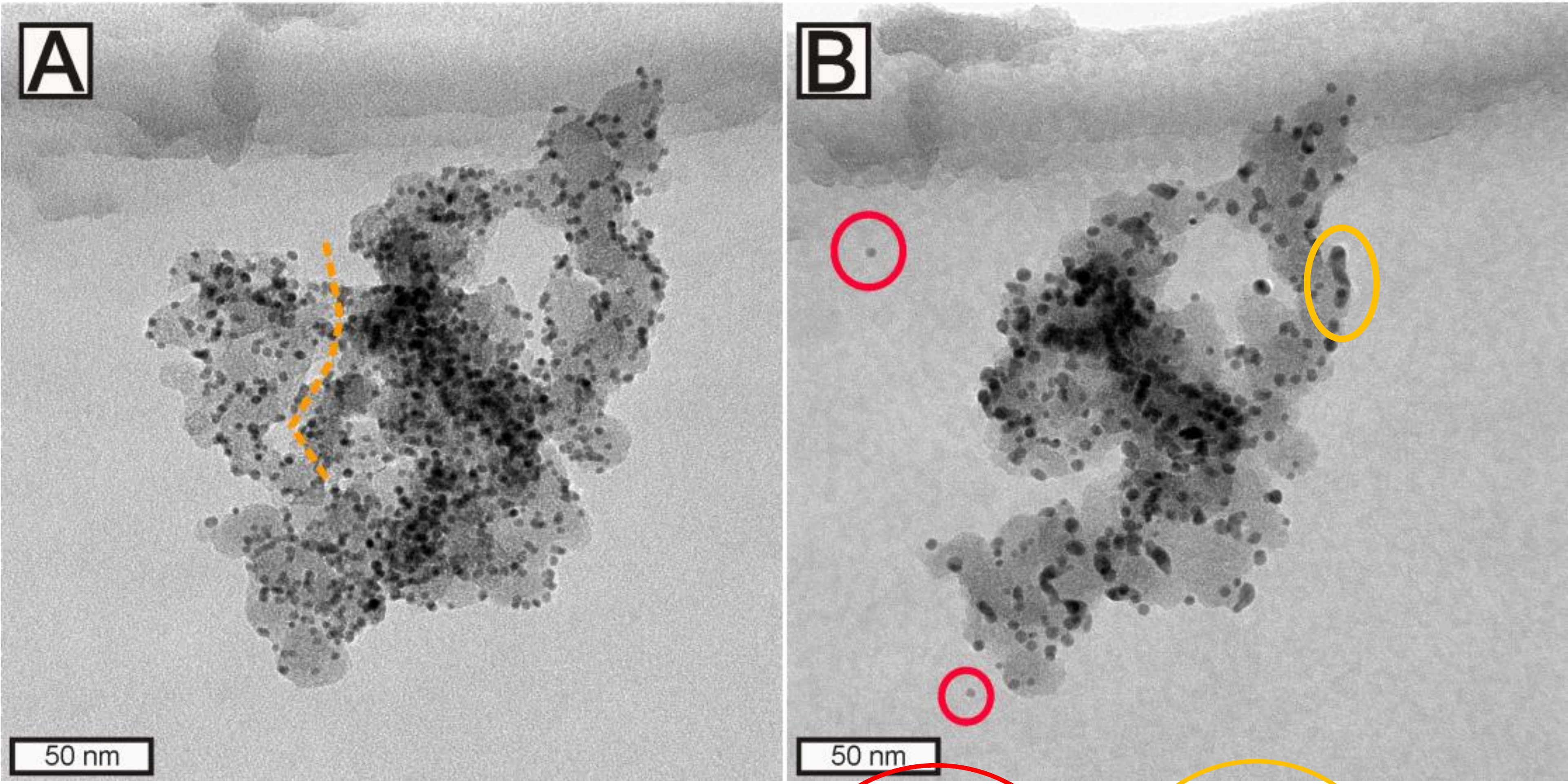
3600 potential cycles, 0.4 – 1.4 V_{RHE}, 0.1 M $HClO_4$, 1 Vs^{-1}

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

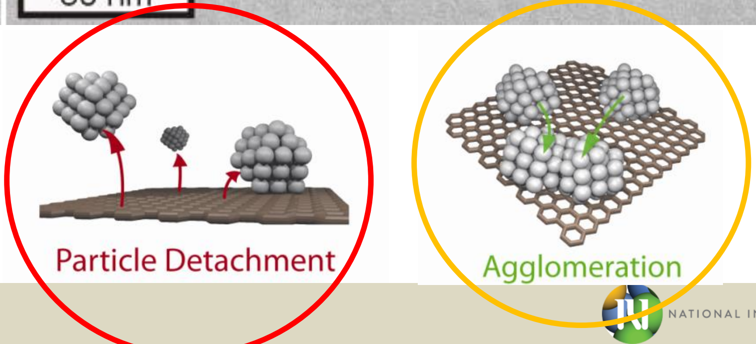


5000 degradation cycles between 0.4 and 1.4 VRHE in 0.1 M HClO4 at a scan rate of 1 V s-1 at room temperature.

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



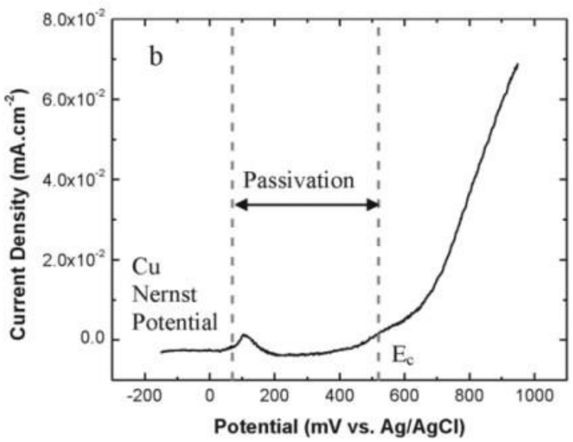
5000 degradation cycles between 0.4 and 1.4 VRHE in 0.1 M HClO4 at a scan rate of 1 V s-1 at room temperature.



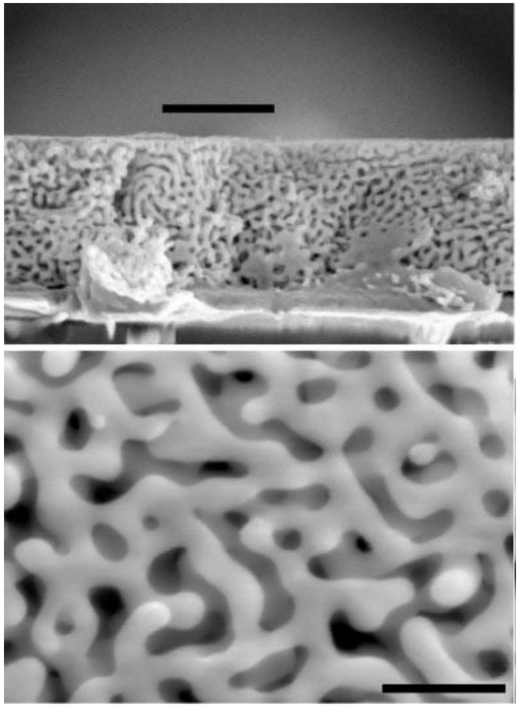
Meier, *ACS Catalysis,* **2012**, 2, 832-843.

Dealloying is selective removal of less noble metal.

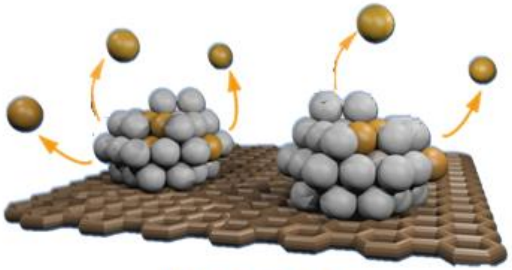
”It is a competition between surface diffusion of noble metal (Pt) and tendency of less noble metal (Cu) to dissolve.”

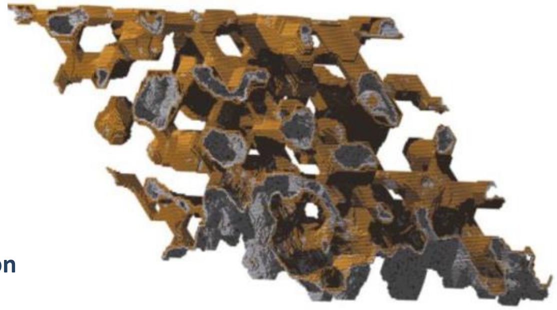


R. Yang et al, J. Phys. Chem. C 115 (2011) 9074–9080.



–> pore formation

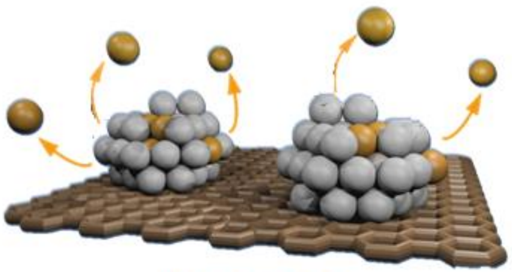




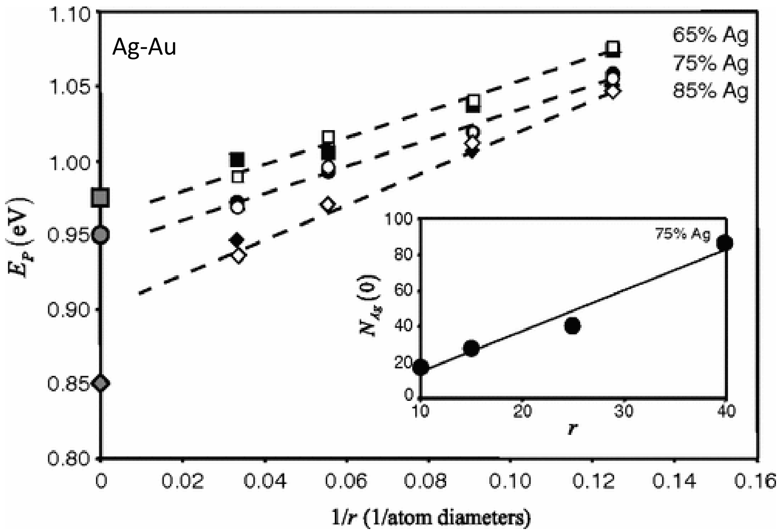
J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, and K. Sieradzki, Nature (London) 410, 450 (2001).

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:

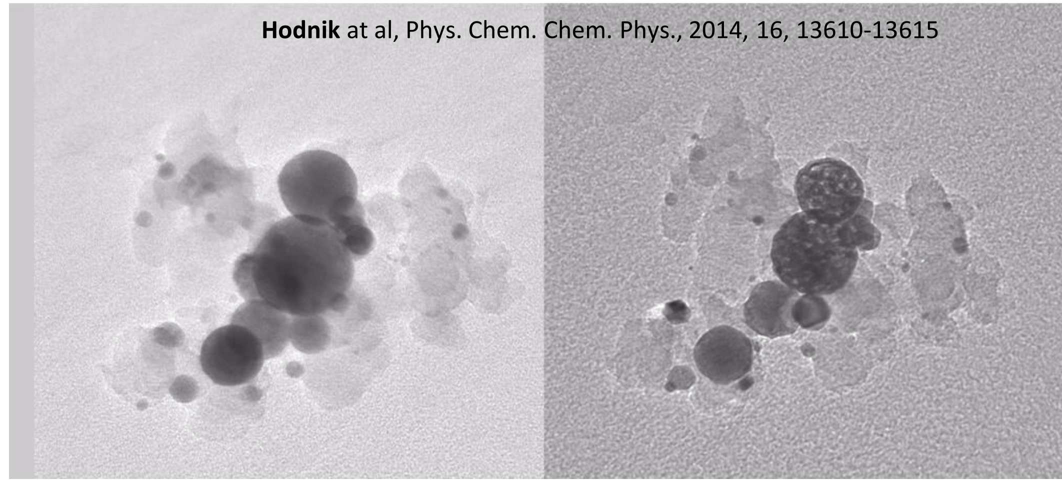


Simulation and model data for the potential for porosity evolution E_P versus of 1/r.

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

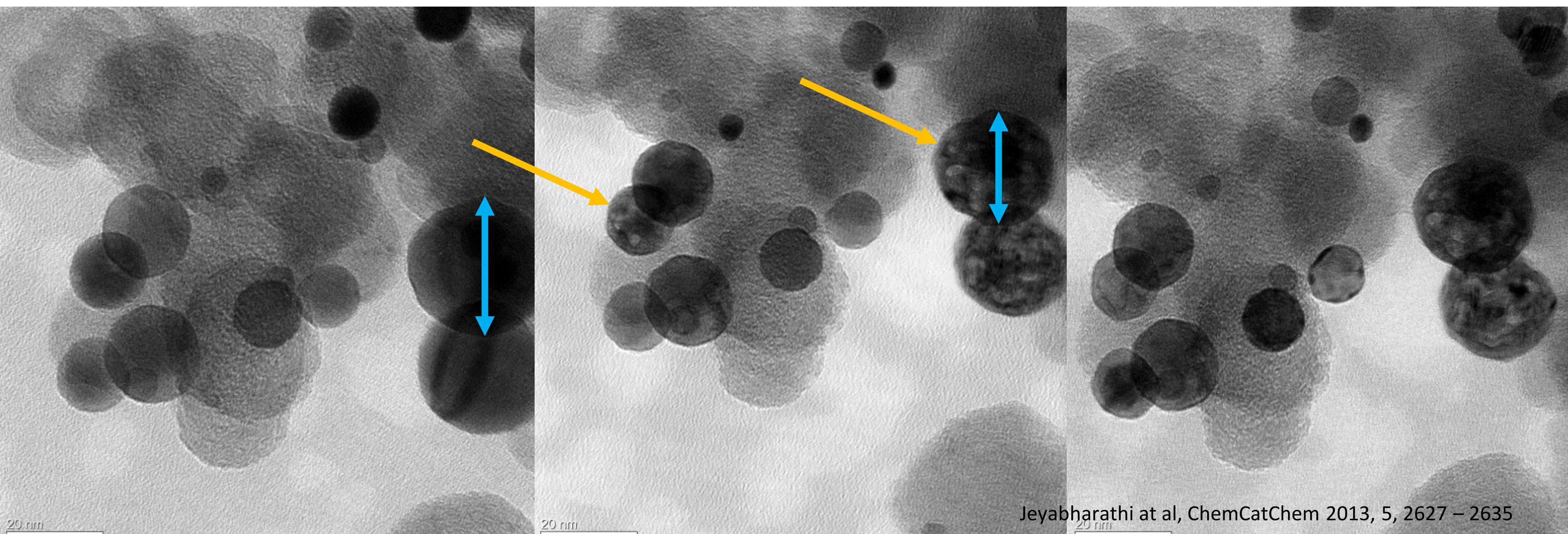


Before dealloying

~60-75 % of Cu removed

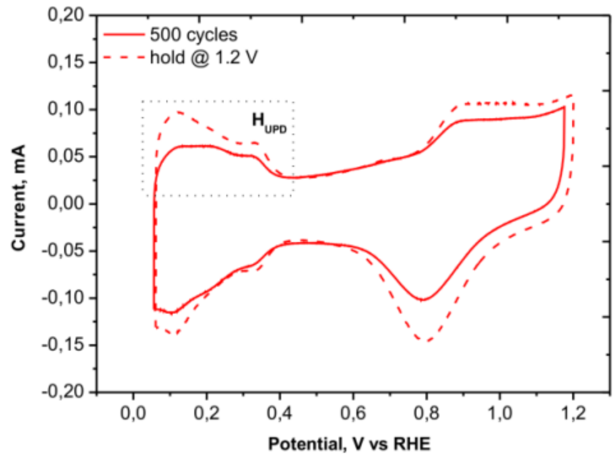
Hold at 1.2V for 2 Hrs

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



NEJC HODNIK

Cyc. Up to 1.2 V $PtCu_3$



-Cubo Octahedron
-Truncated Octahedron
-Cube
-Tetrahexahedral

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

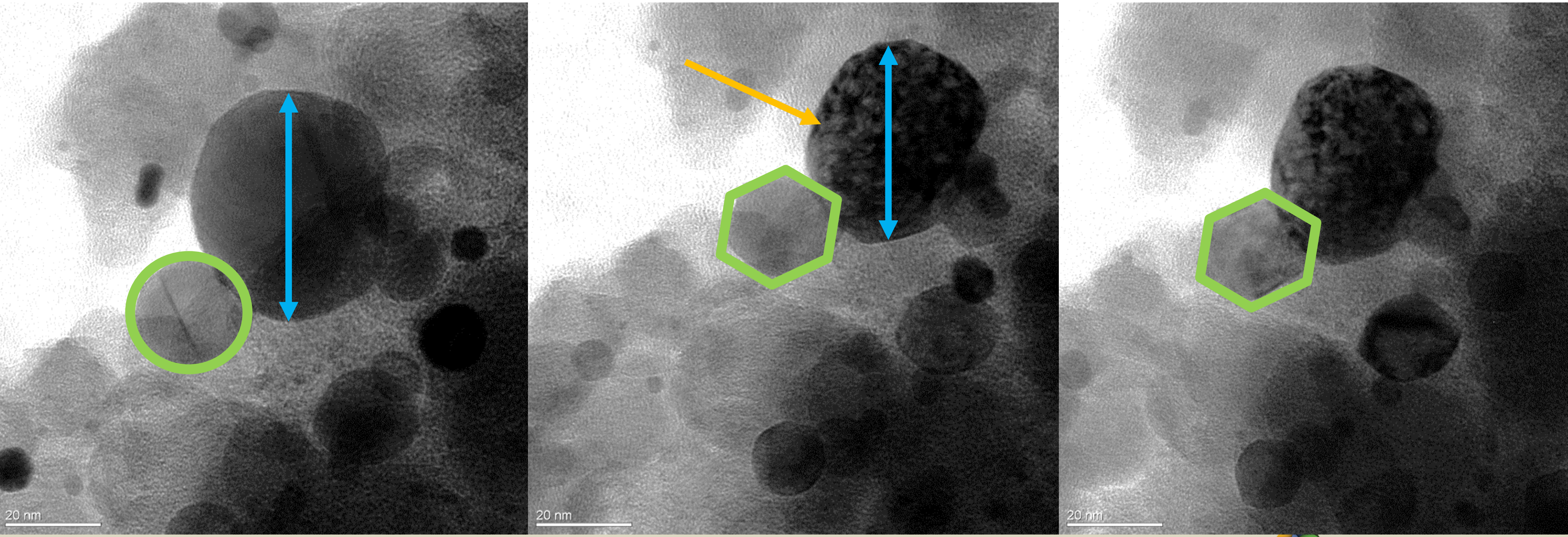
–0.10 and –0.20 V to 1.20 V vs. SCE

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

Before dealloying

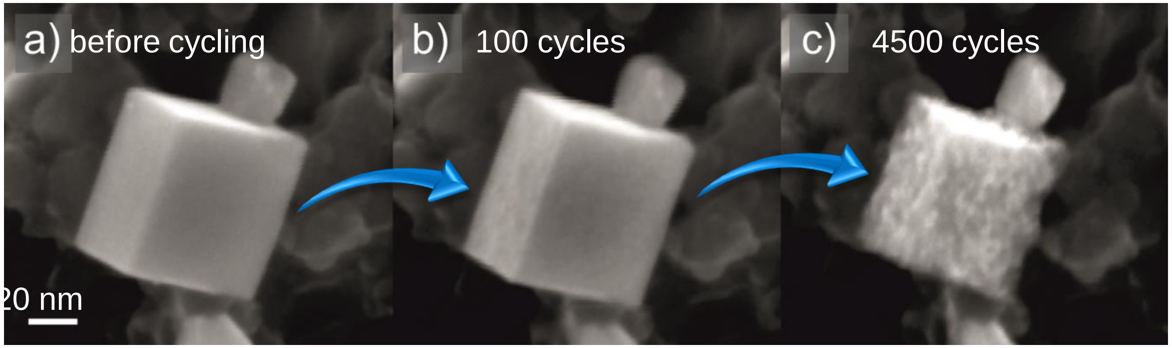
Cycling: 0.05 to 1.2 V, scan rate=0.5 V/s; 500 cycles (2 Hrs)

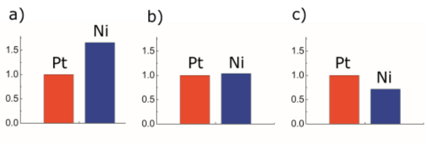
Cycling: 0.6 to 1.2 V, scan rate=1 V/s; 7000 cycles



NEJC HODNIK

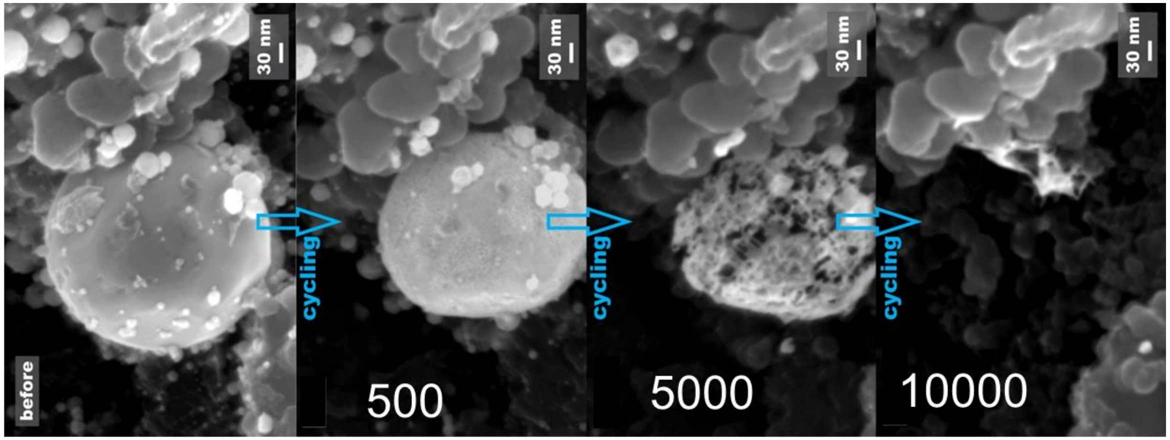
NiPt





IL-SEM-EDX

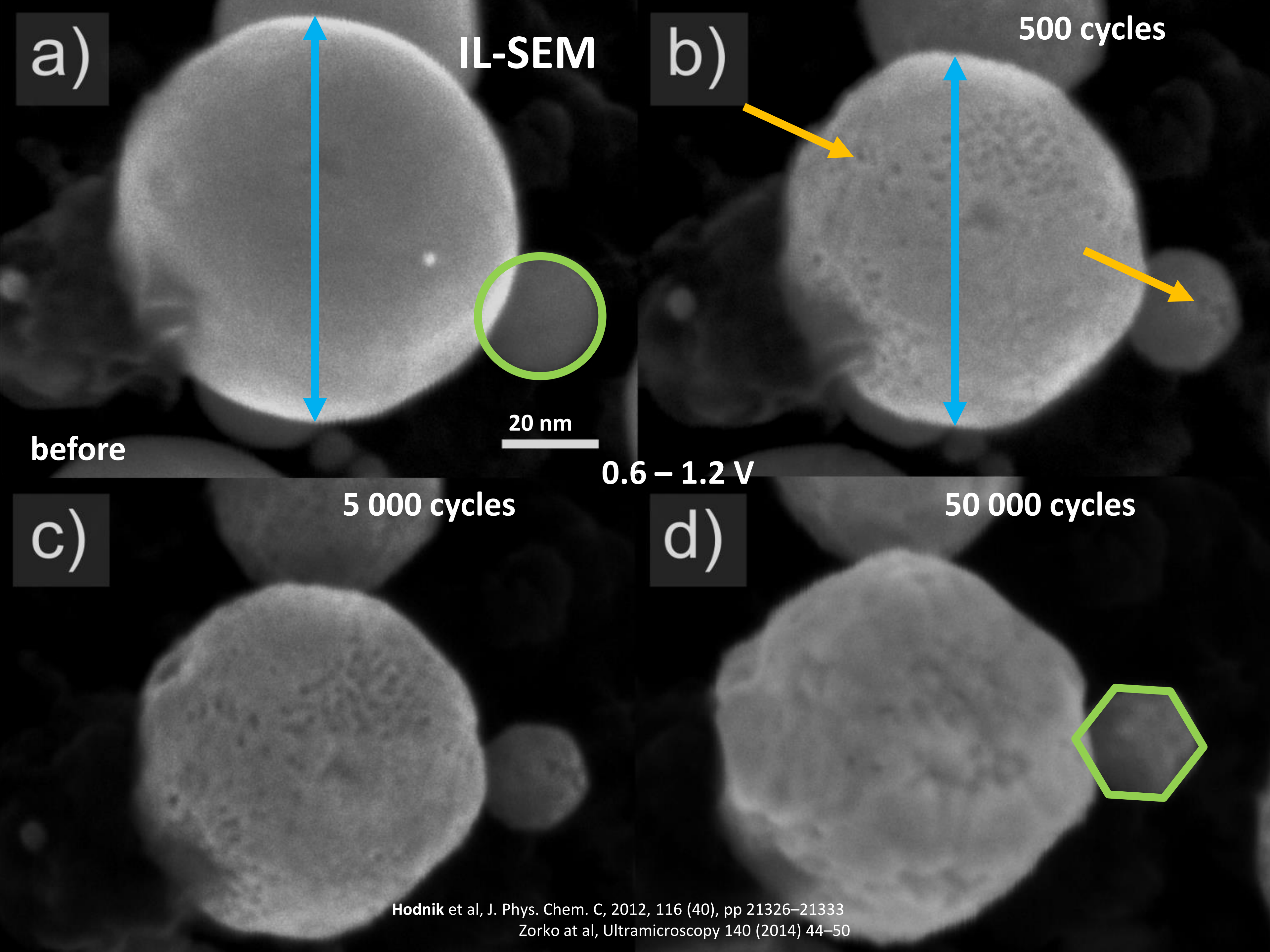
Cu_3Pt



SEM Microsope (HI-resolution):
FE-SEM Zeiss SUPRA 35VP

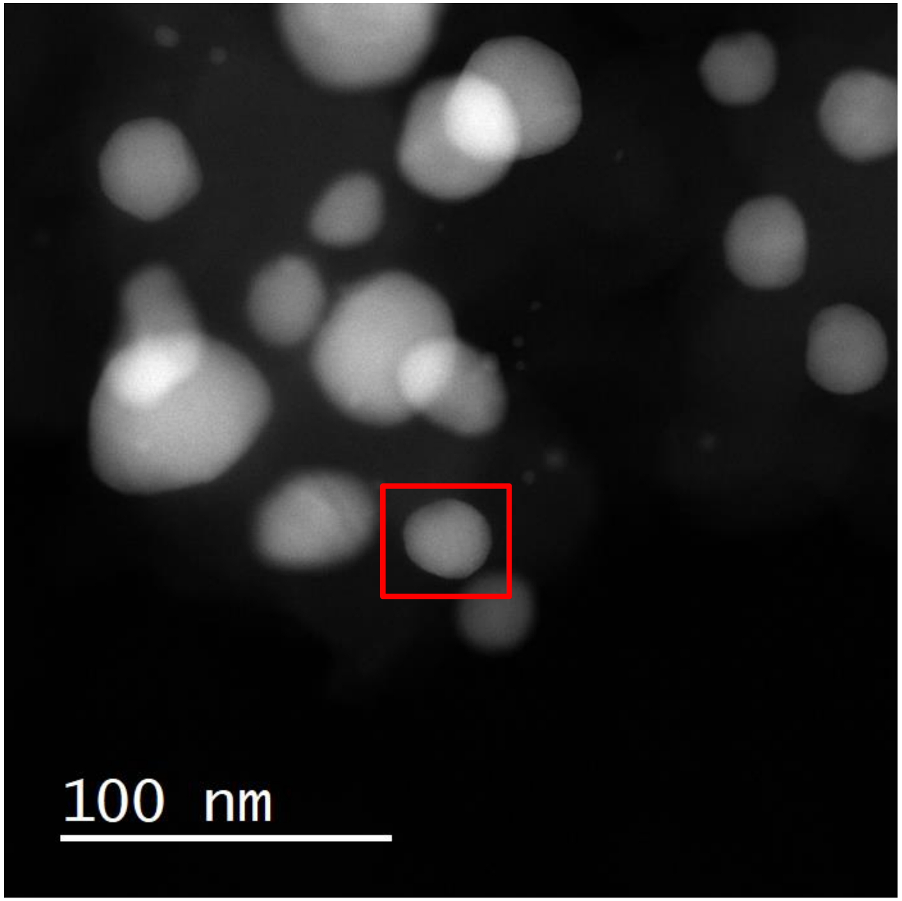
- Utilizing versatile SEM graphite holdes or any other conductive sample
- Enabels visual tracking of nanoscale morphological changes upon any treatment

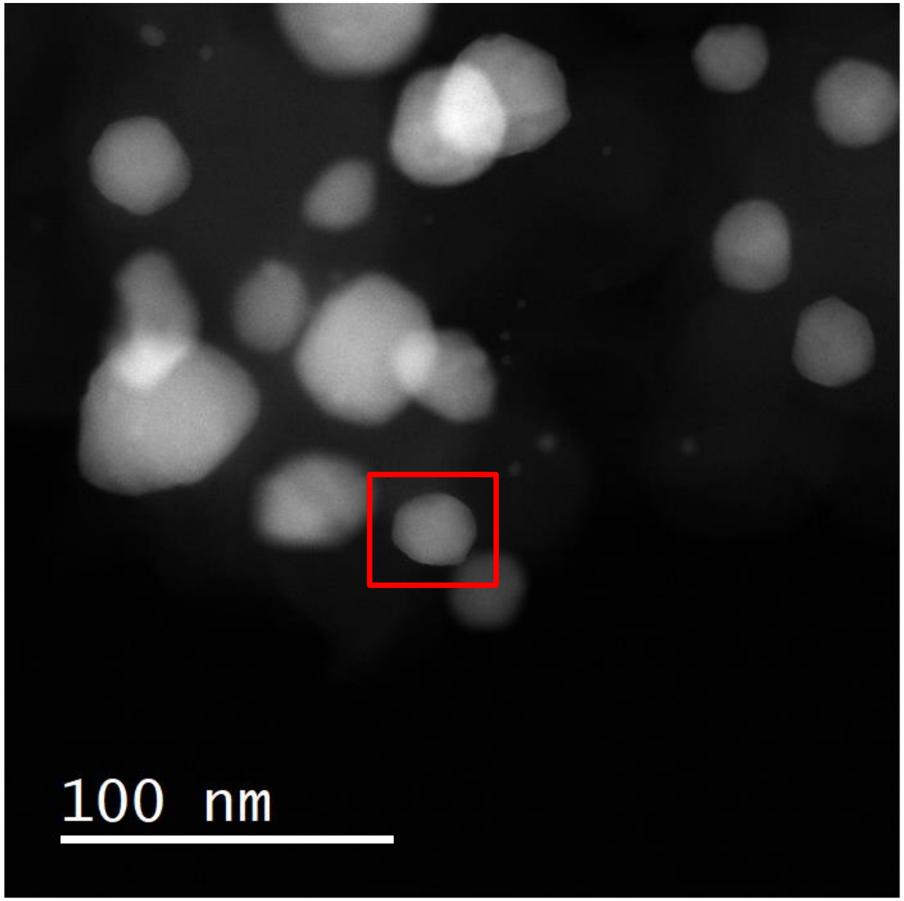
Hodnik, J. Phys. Chem. 2012, 116, 21326



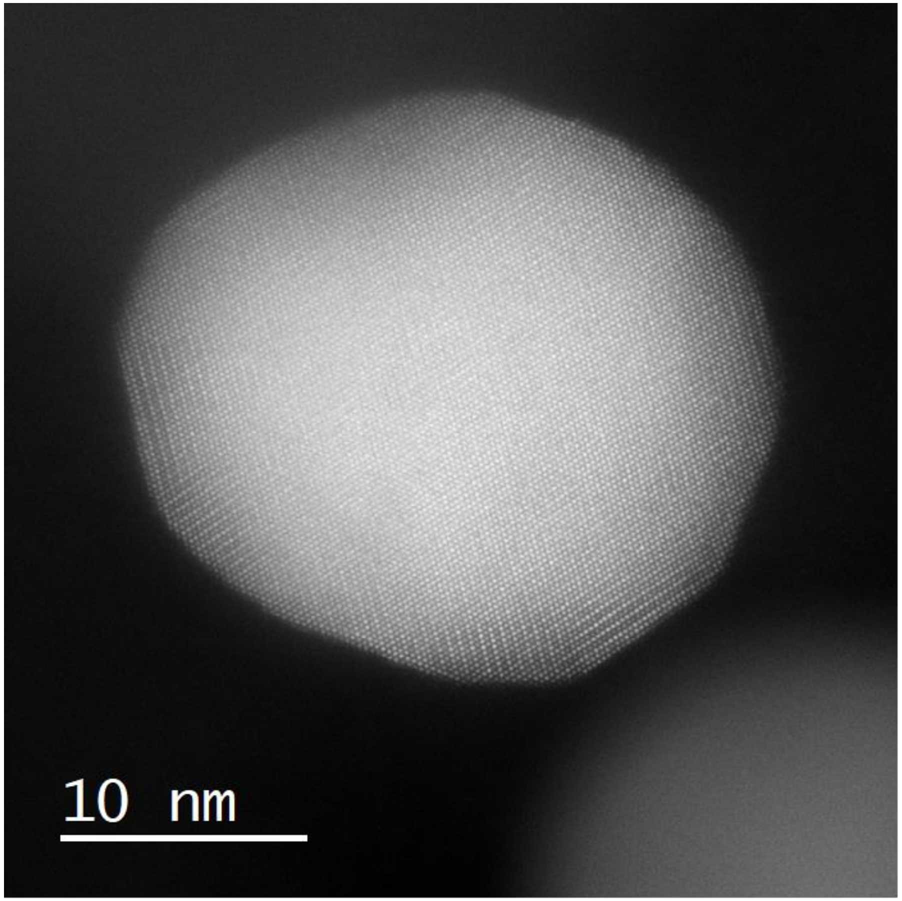
Hodnik et al, J. Phys. Chem. C, 2012, 116 (40), pp 21326–21333
Zorko at al, Ultramicroscopy 140 (2014) 44–50

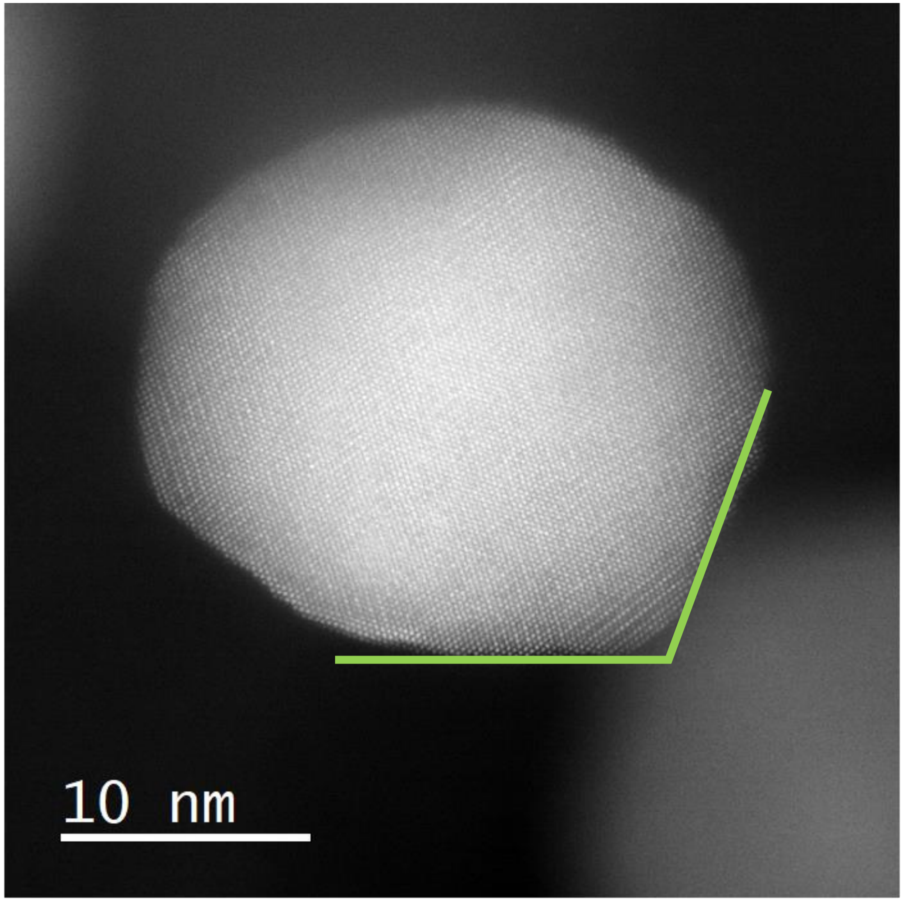
NEJC HODNIK



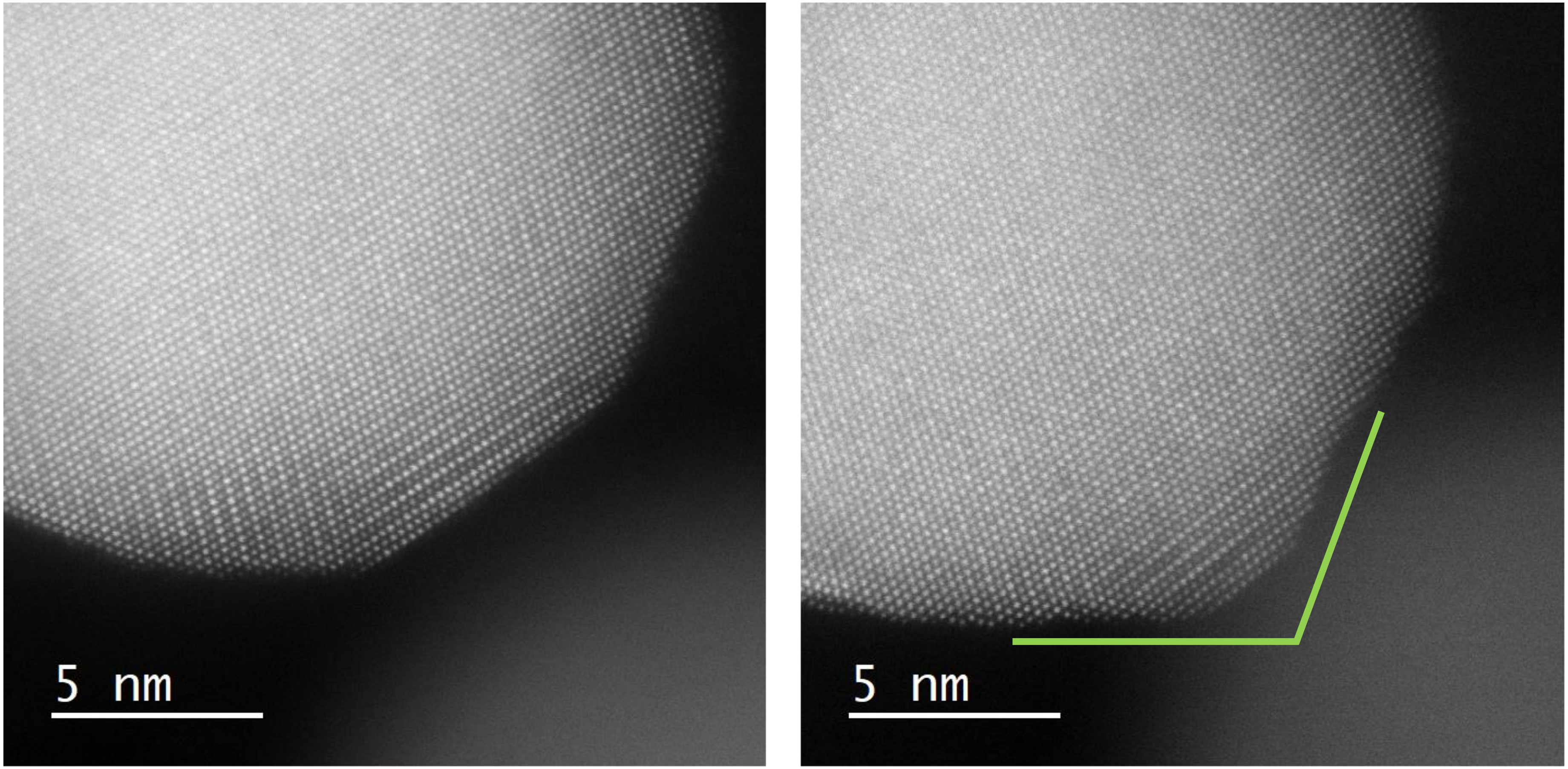


unpublished



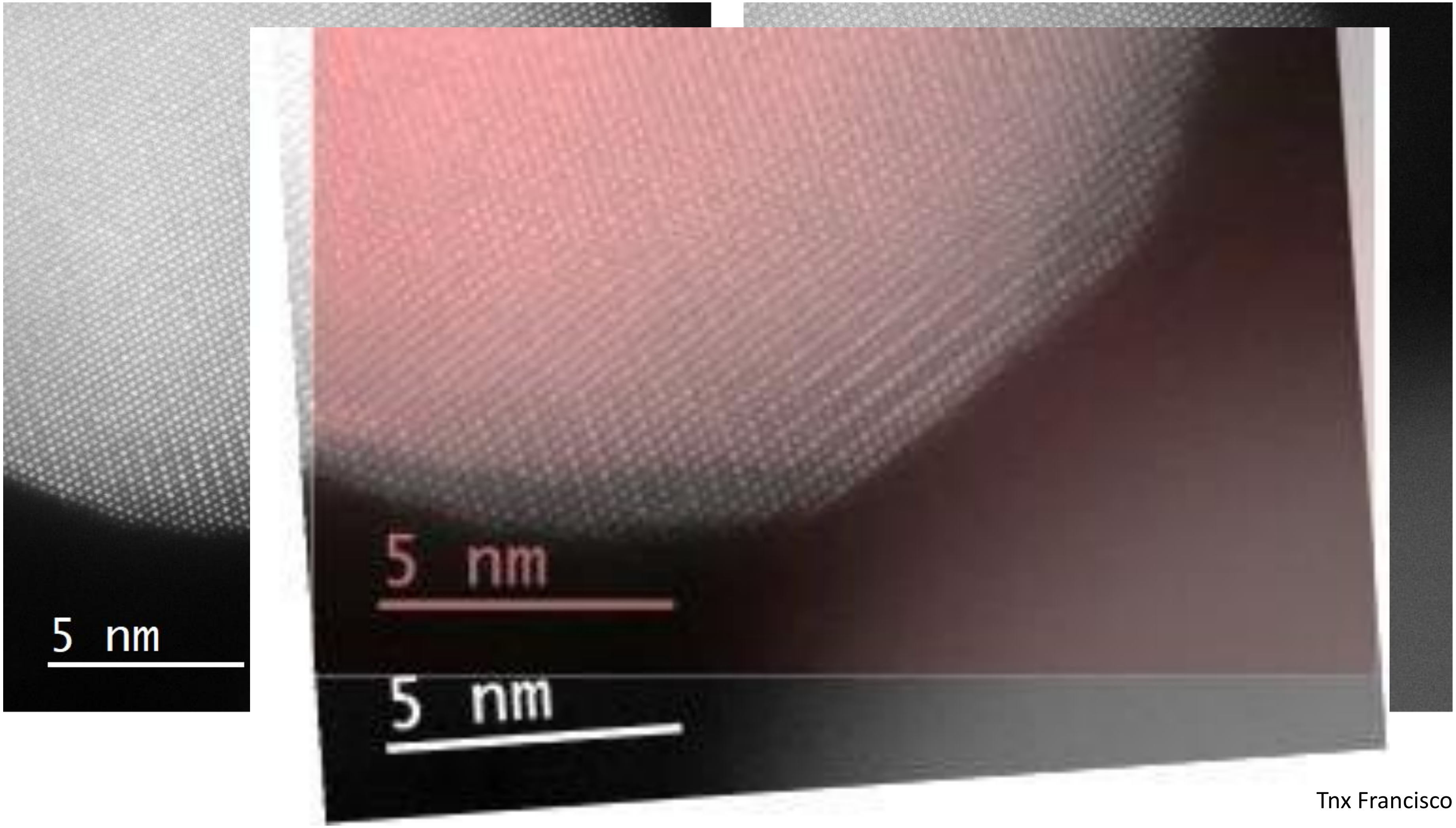


unpublished



Tnx Francisco

unpublished



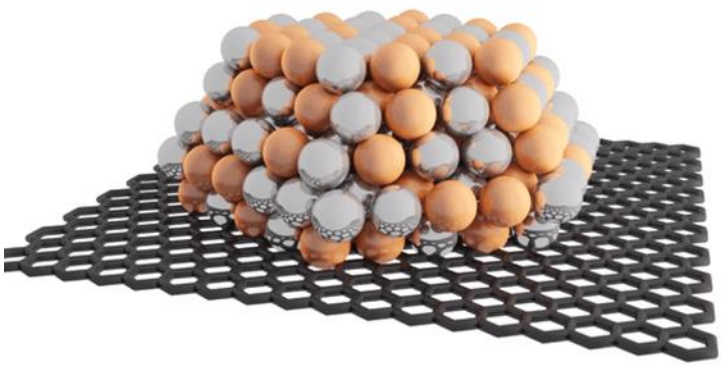
Tnx Francisco

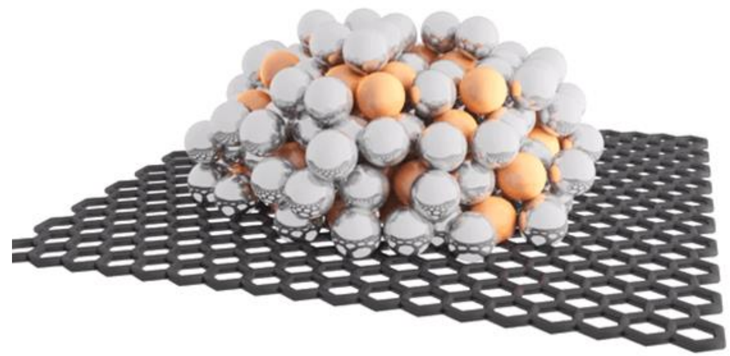
unpublished

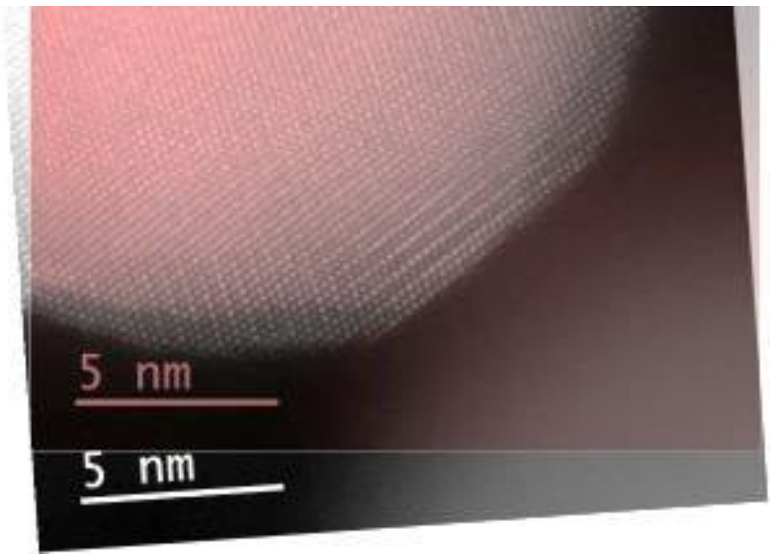
NEJC HODNIK

Forum40, Maj 2018, Ljubljana

Atomic-scale atoms diffusion of NM nanoparticles changes in liquid enviroments





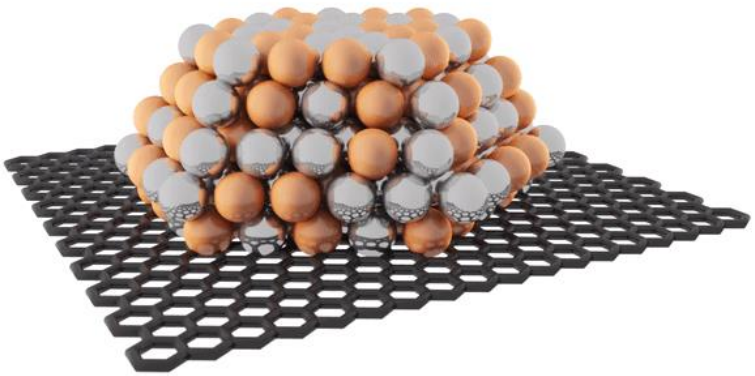


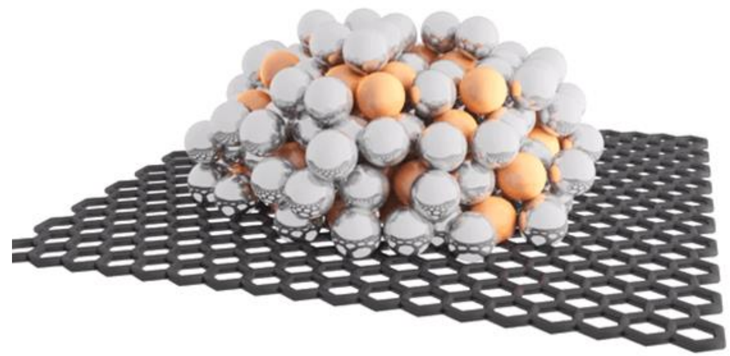
unpublished

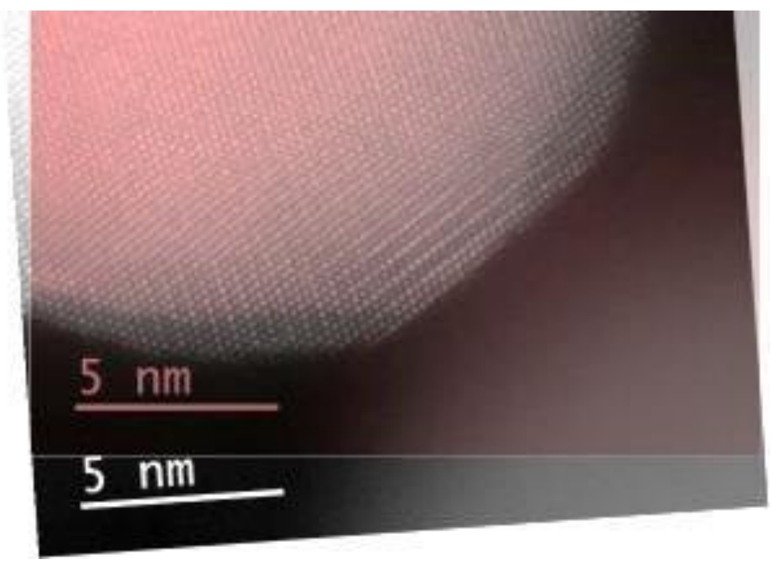
NEJC HODNIK

Forum40, Maj 2018, Ljubljana

Atomic-scale atoms diffusion of NM nanoparticles changes in liquid enviroments

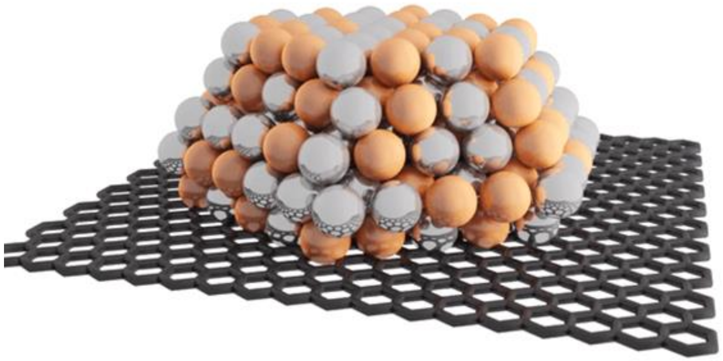


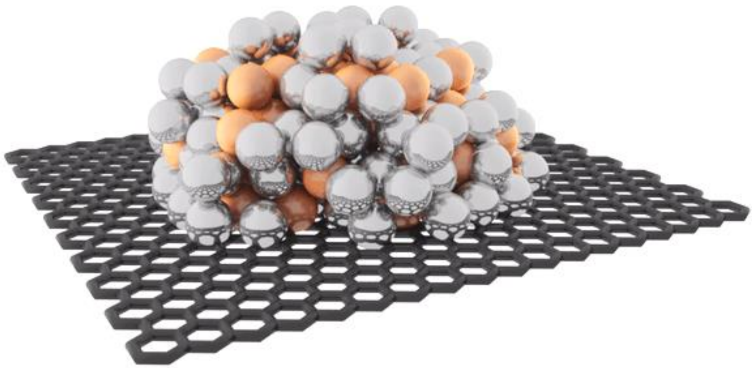


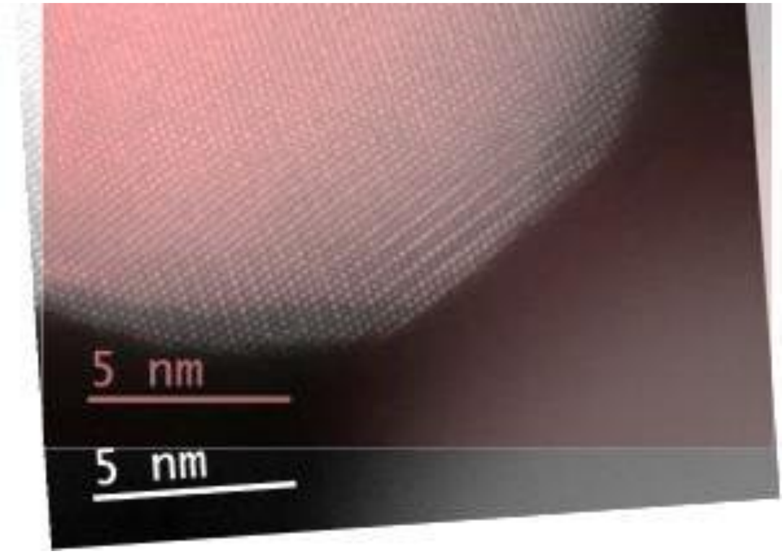


unpublished

Atomic-scale atoms diffusion of NM nanoparticles changes in liquid enviroments



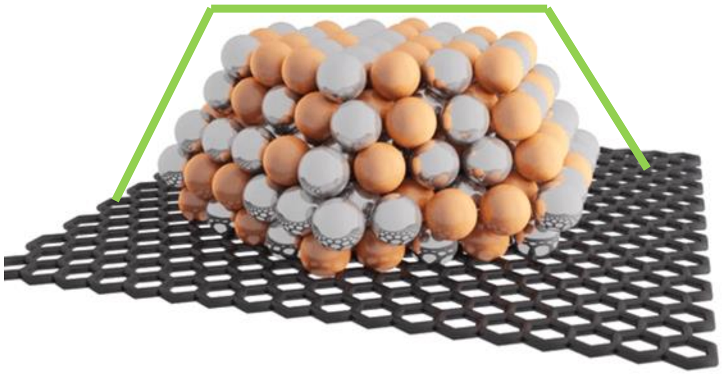


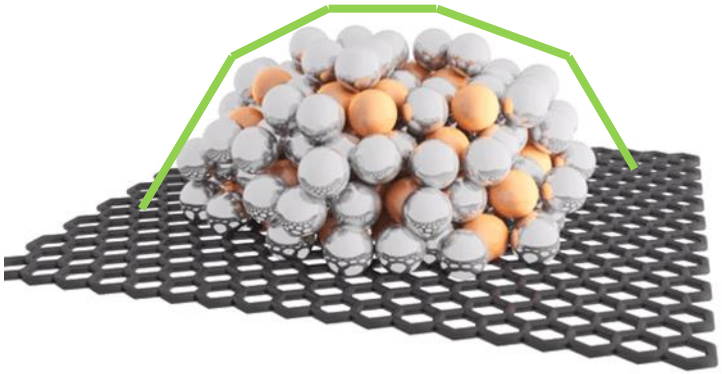


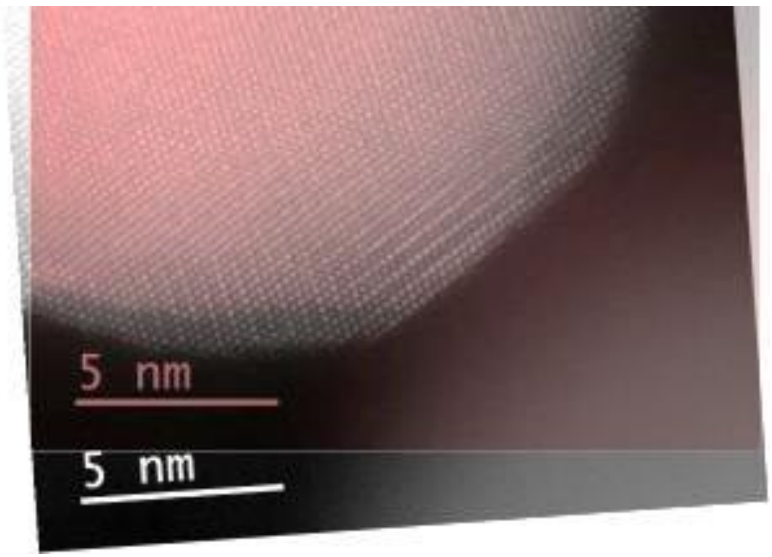
unpublished

NEJC HODNIK

Atomic-scale atoms diffusion of NM nanoparticles changes in liquid enviroments

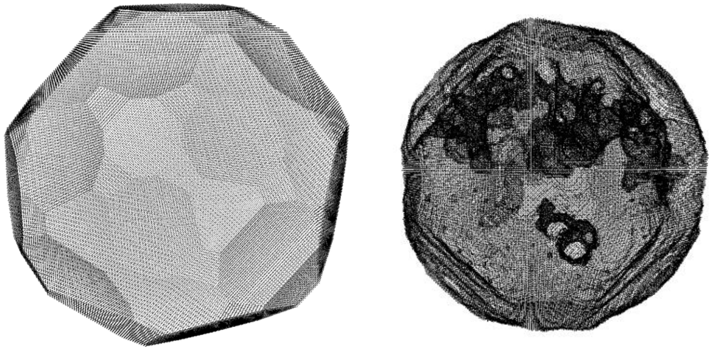






We need 3D insights!

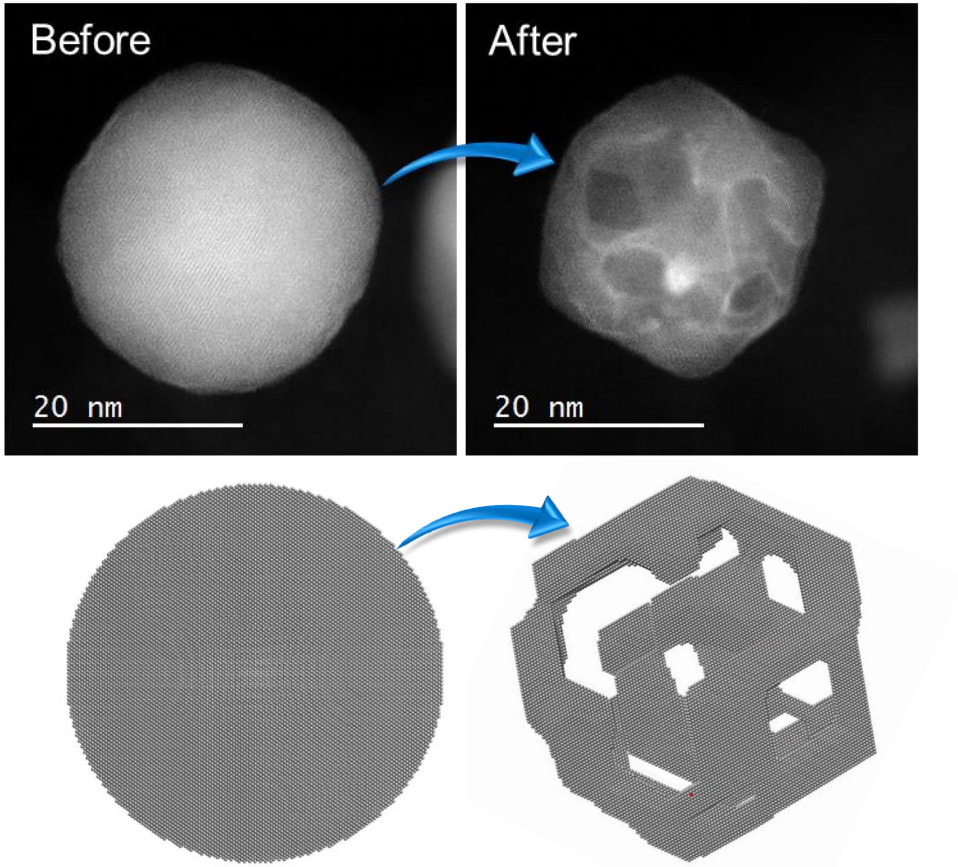
- TEM Tomography
- 3D atomic simulations



Tnx Andraž

unpublished

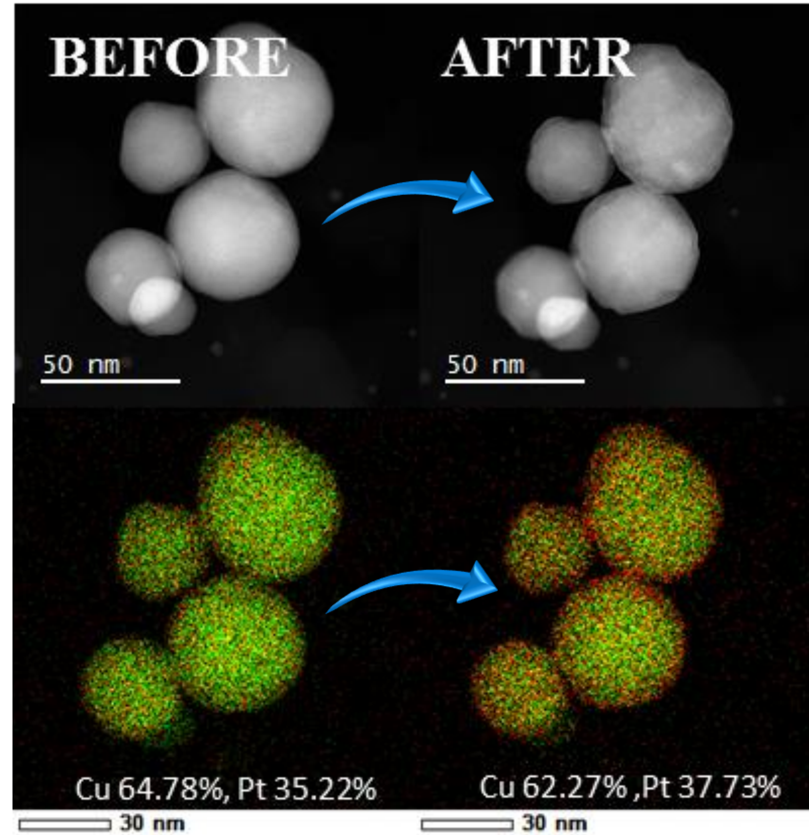
$PtCu_3$ dealloying – selective Cu dissolution



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

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

$PtCu_3Au$ dealloying



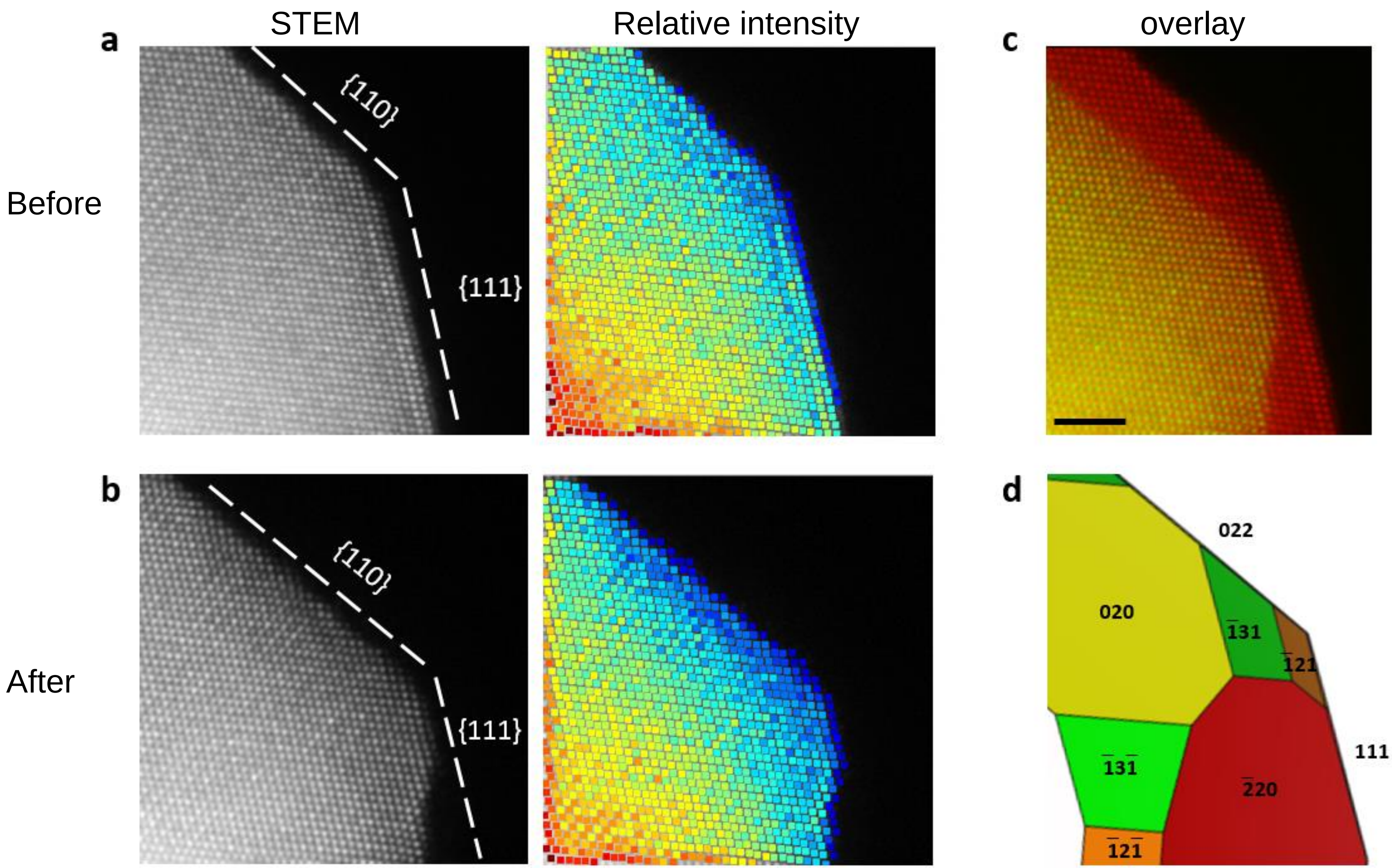
IL-STEM-EDX

-we can use any other detector available in the TEM

Zepeda, Hodnik, accepted in ChemCatChem, 2017
Gatalo, Hodnik, J. Electrochem. Sci. Eng., 2018, 8 (1) pp. 87-100

NEJC HODNIK

Example 1

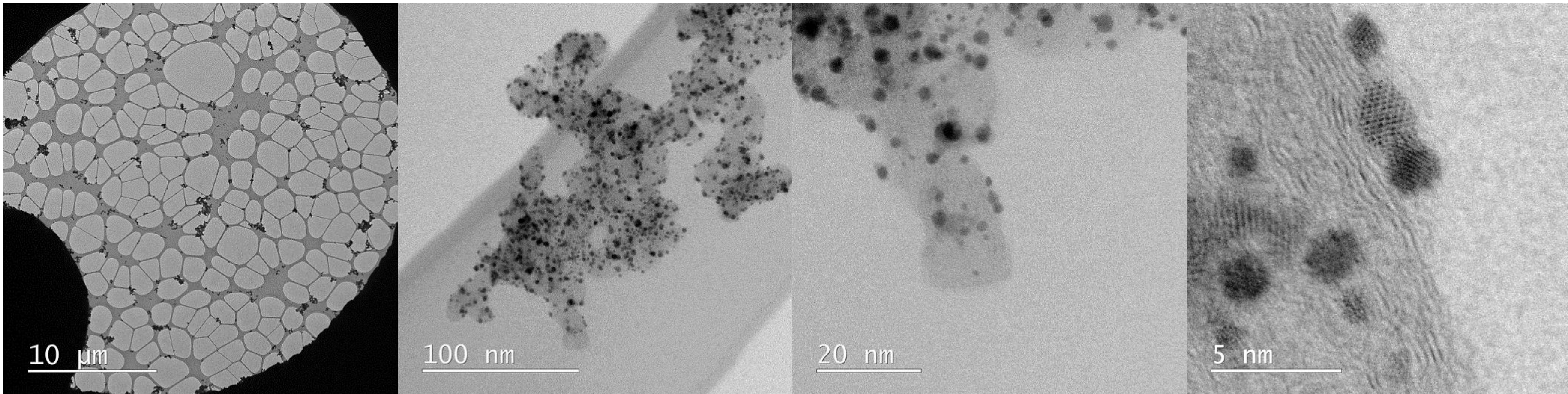


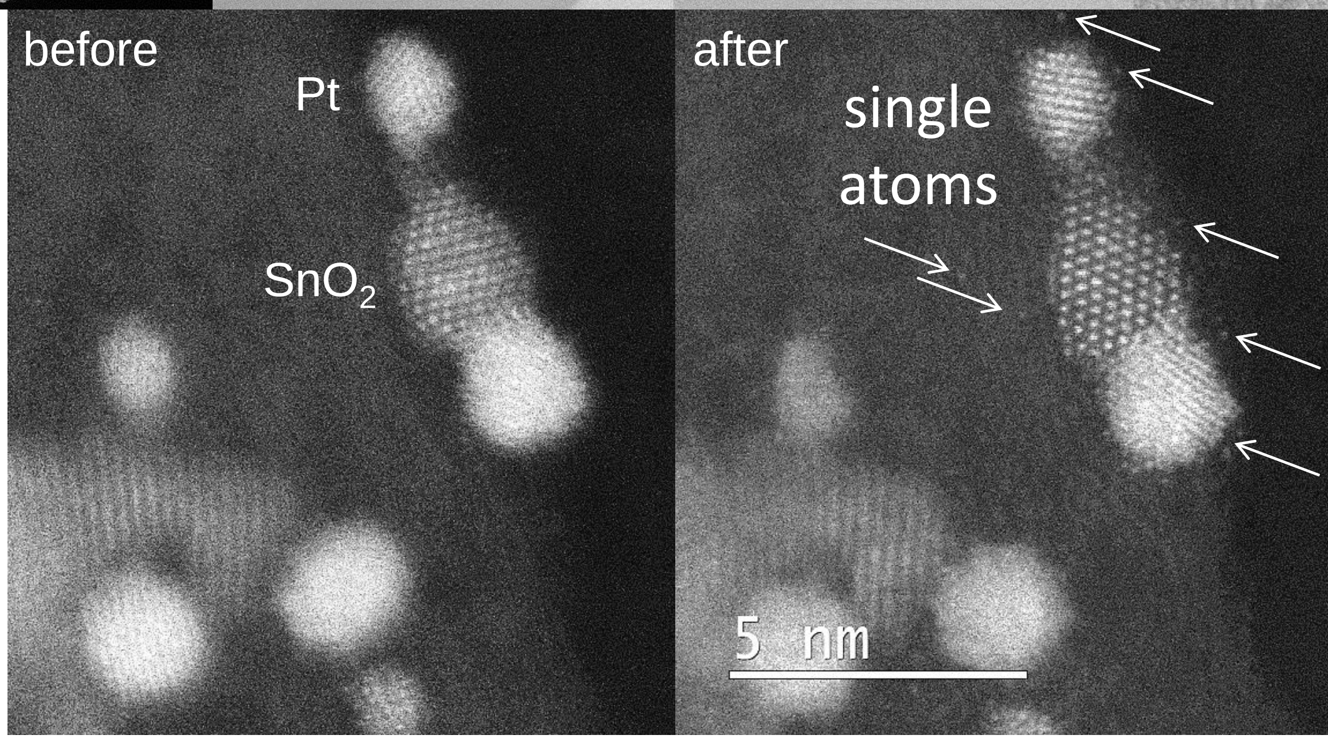
Tnx Francisco

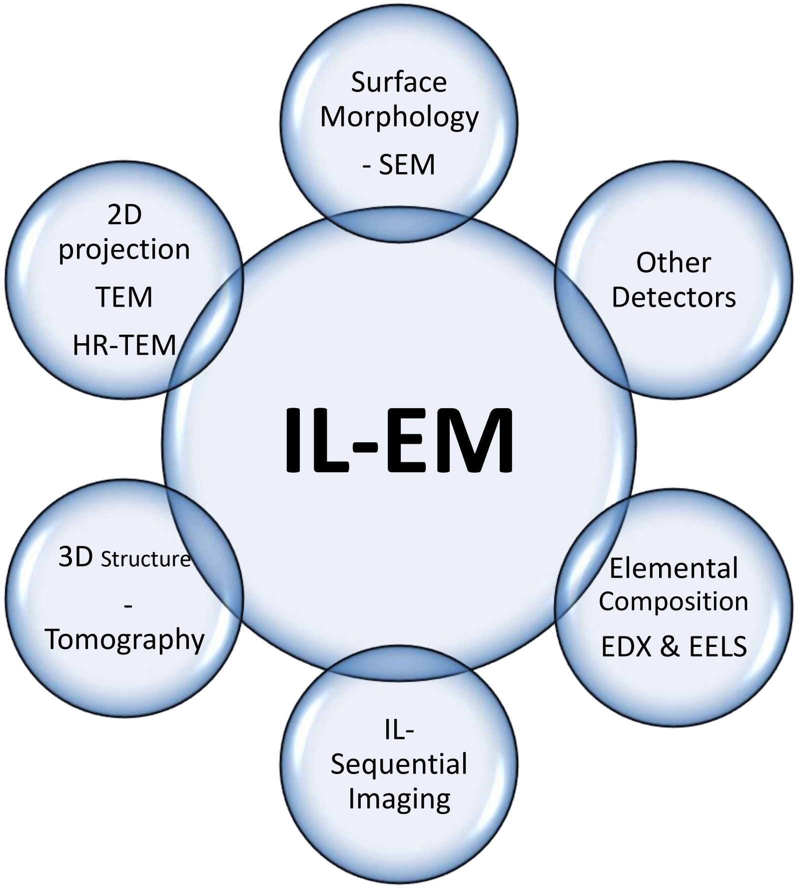
unpublished

NATIONAL INSTITUTE OF CHEMISTRY

Example 2

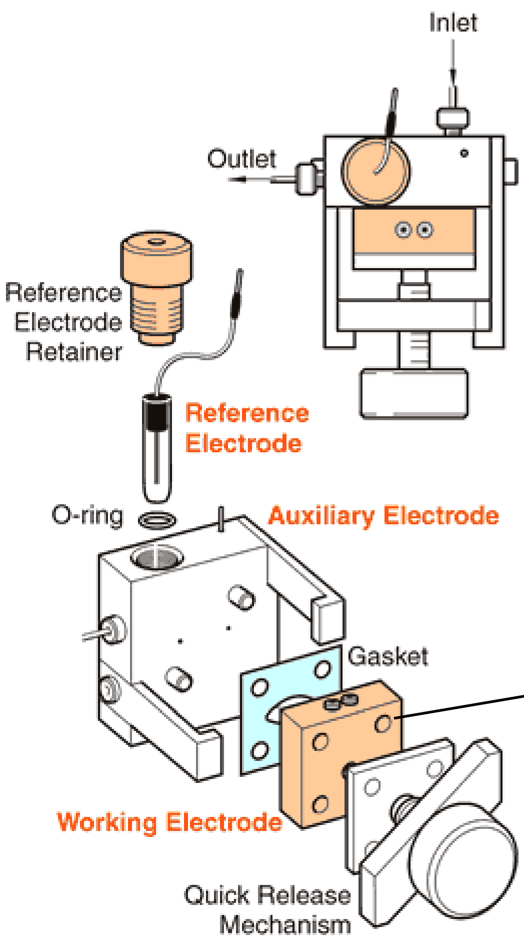


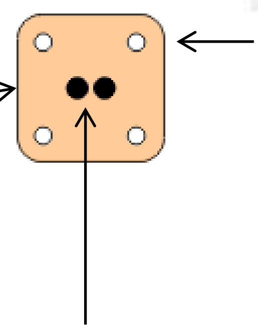




-other materials
-synthesis
-heterogeneous catalysis
-any kind of treatment

We have structure! Now how to measure dissolution?



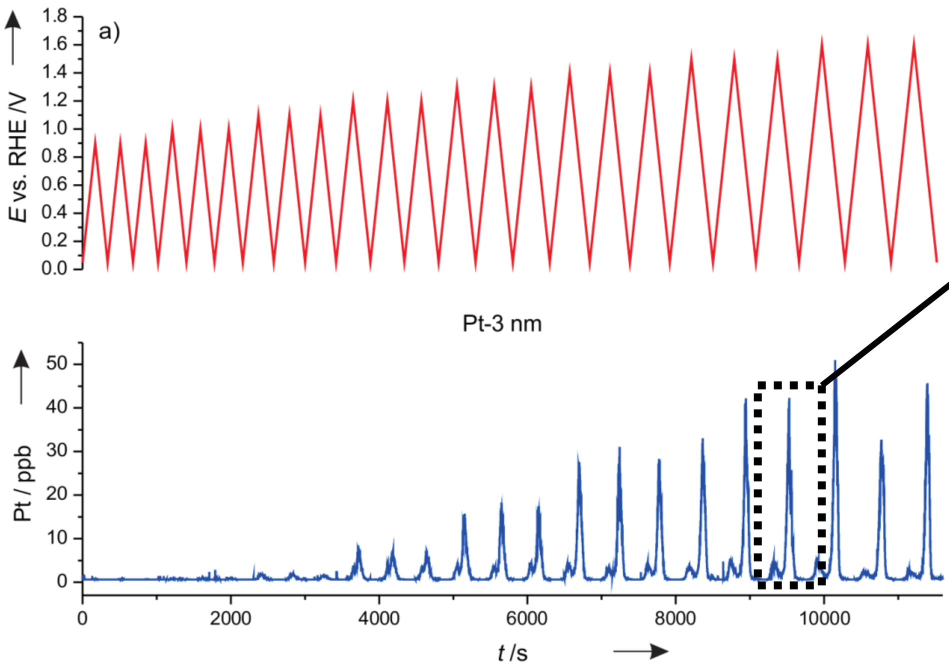


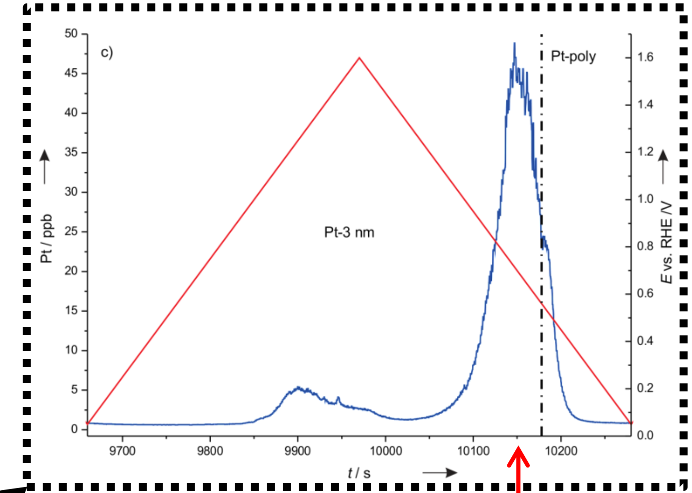
- -many different electrolytes
- -can couple to ICP-MS and ICP-OES
- -either peristaltic pump of syringe
- -can analyze corrosion of any metallic samples

http://www.basinc.com/products/ec/flowcells.php

Extremely sensitive potential- and time- resolved dissolution profiles of metals

PEM Fuel Cell catalyst: Pt 3 nm





„transient dissolution“

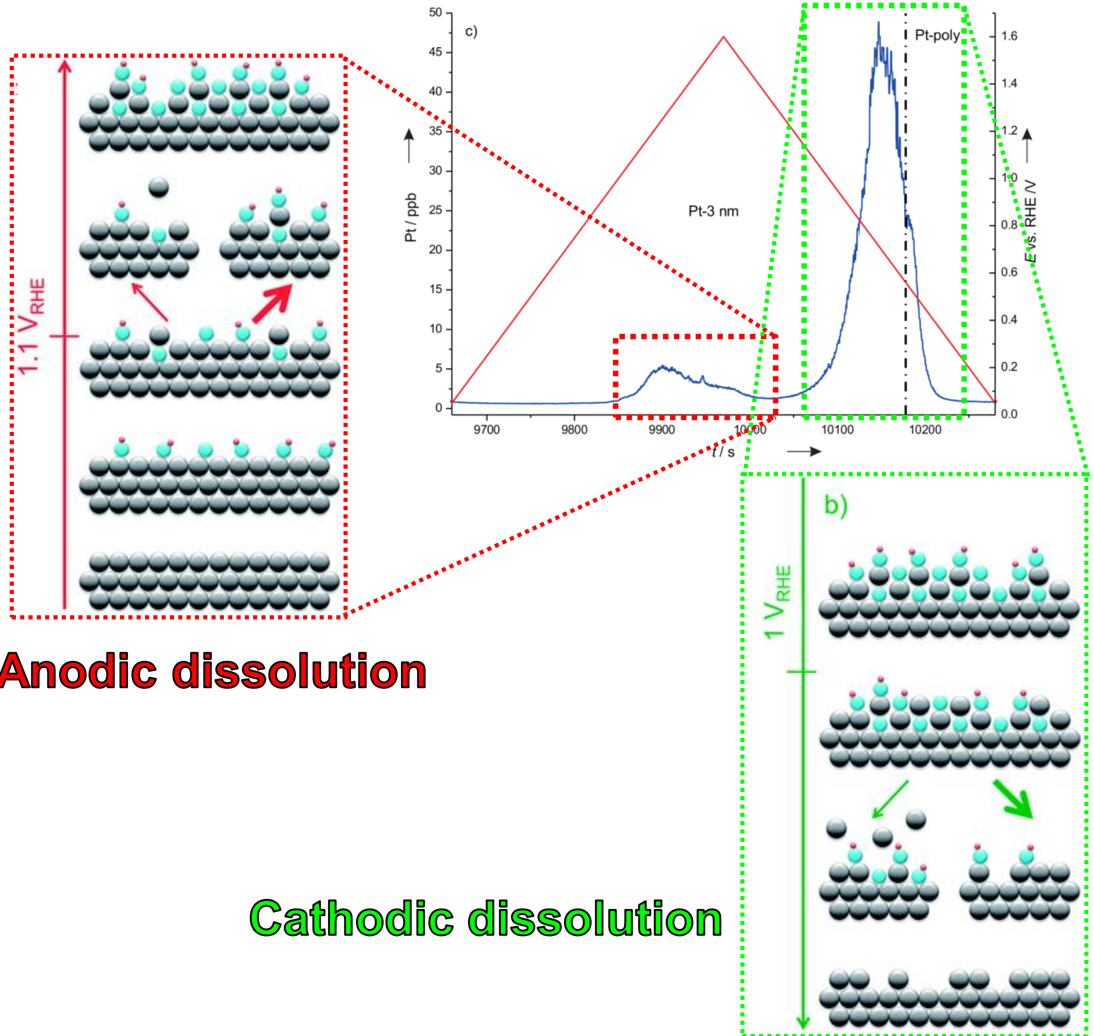
1. **Similar behavior as Pt-poly**
2. **In one cycle with vertex limit 1.6 V:**

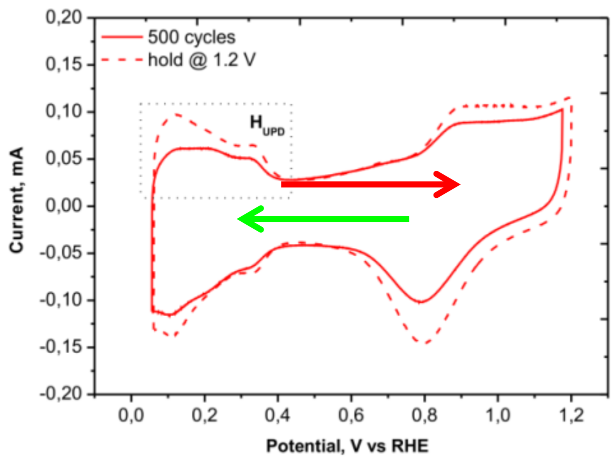
Pt/C	0.43%	or	1.4% of a monolayer
Pt/black	0.04%	or	0.7% of a monolayer
$PtCu_3/C$	0.22%	or	1.1% of monolayer

Jovanovic, Hodnik, ChemCatChem, 2014, 6, pps 449–453

Extremely sensitive potential- and time- resolved dissolution profiles of metals

PEM Fuel Cell catalyst: Pt 3 nm





NEJC HODNIK

Extremely sensitive potential- and time- resolved dissolution profiles of metals

PEM Fuel Cell catalyst: Pt/C – 3 nm

$-Cl^-$ induced platinum dissolution

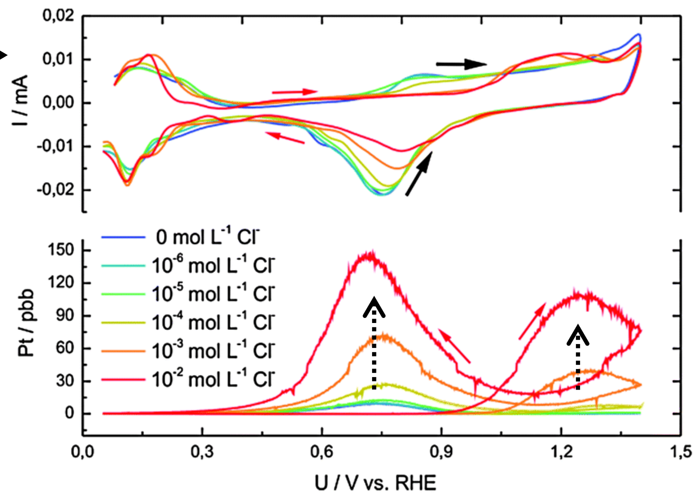
Electrochemistry →

↑

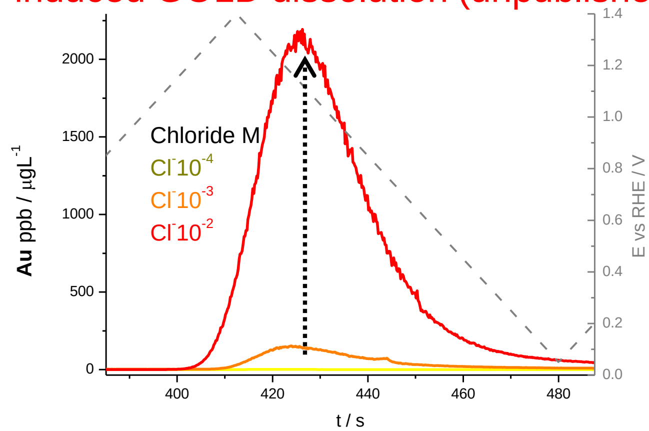
synchronized

↓

ICP-MS signal →



$-Cl^-$ induced GOLD dissolution (unpublished)



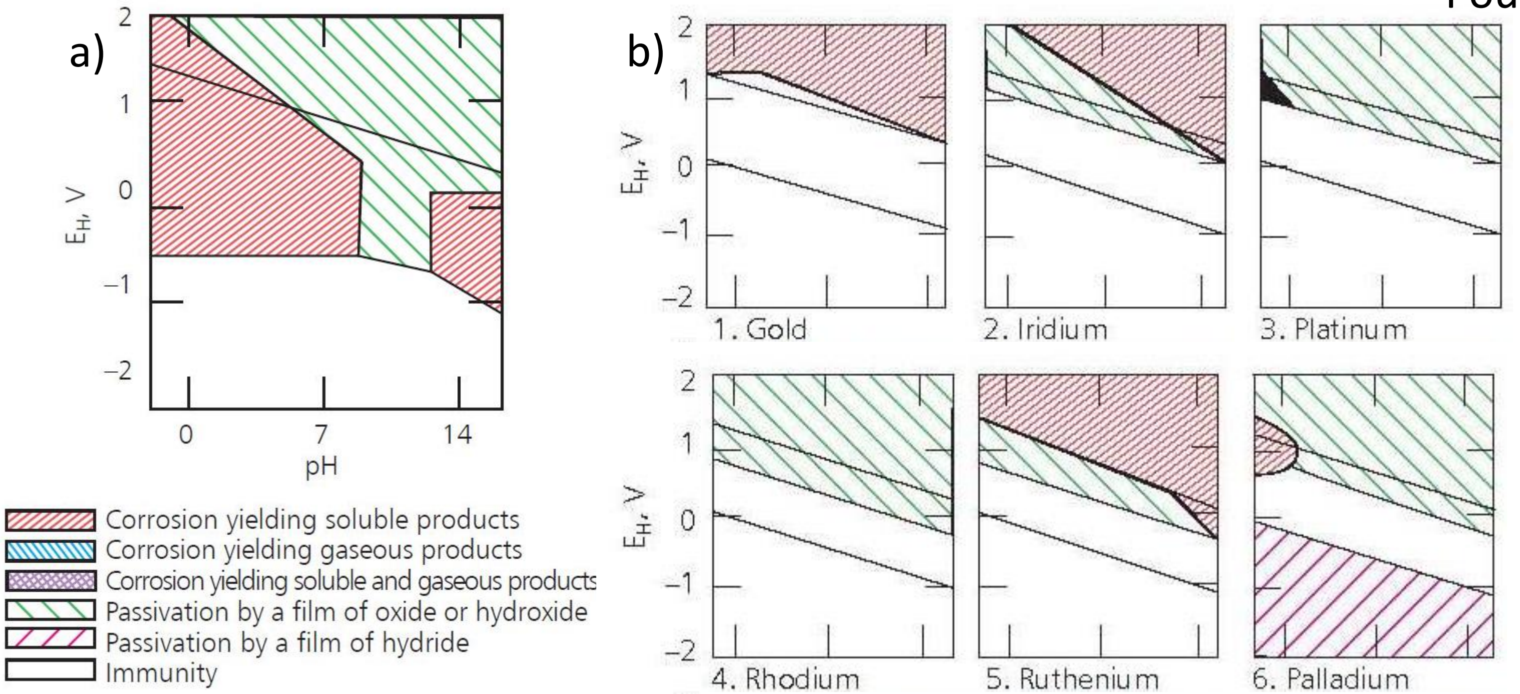
Tnx Primož

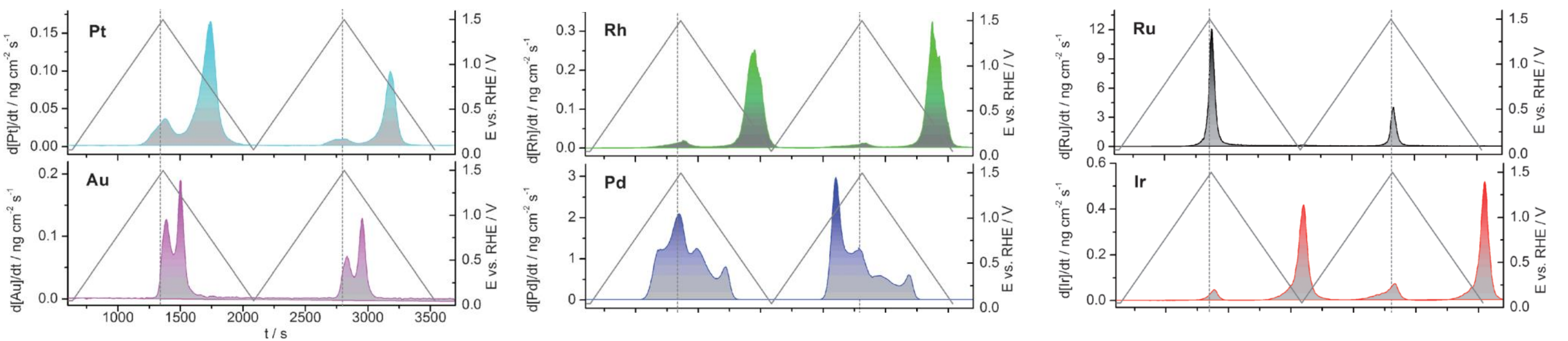
Pavlisic, Hodnik, Chem. Commun., 2014,50, 3732-3734

NEJC HODNIK

Dissolution of PGM

Pourbaix diagrams





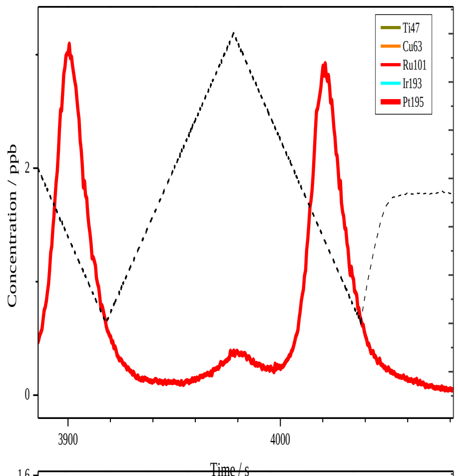
NEJC HODNIK

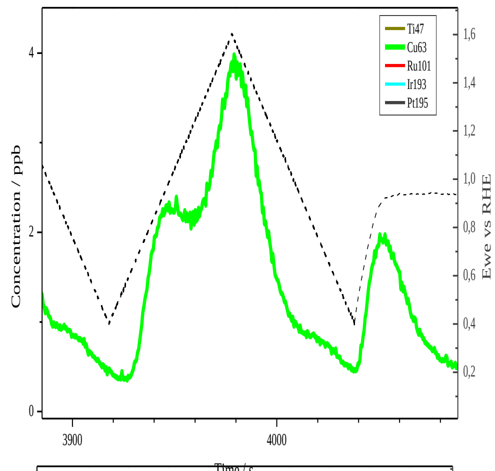
Forum40, Maj 2018, Ljubljana

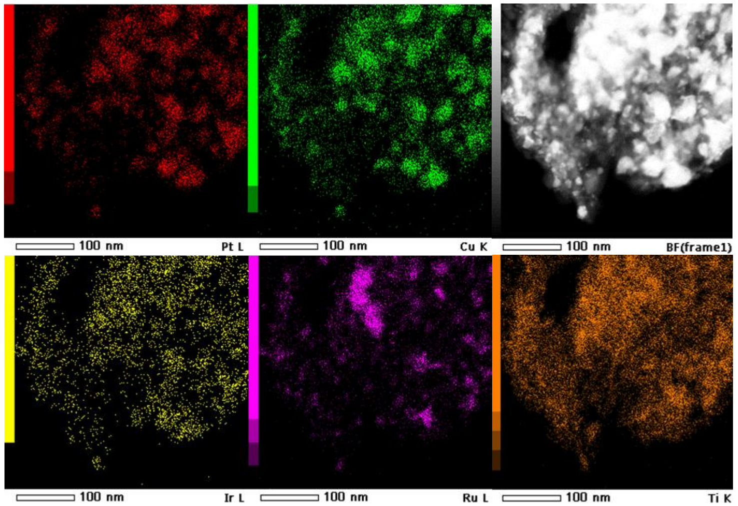
Dissolution of PGM

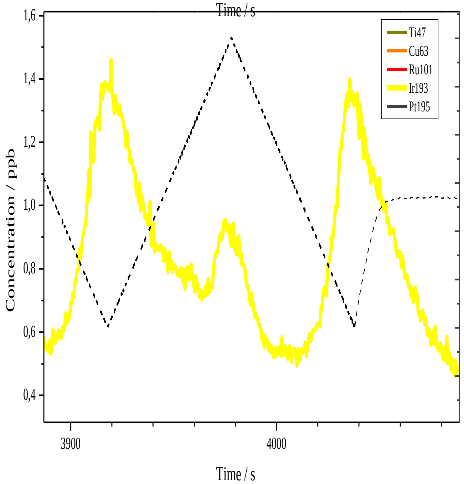
“all-in-one“ or a good electrocatalyst for everything

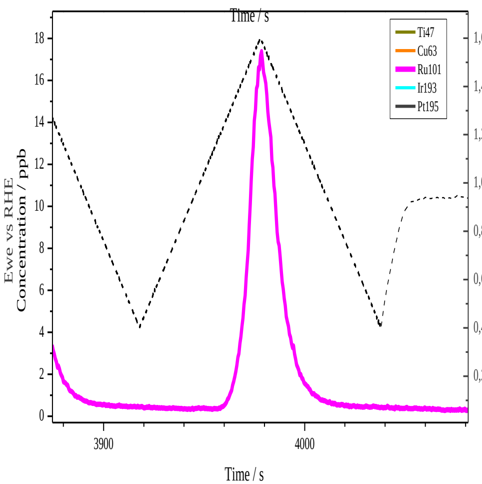
Pt, Cu, Ir, Ru, Ti, C nanocomposite

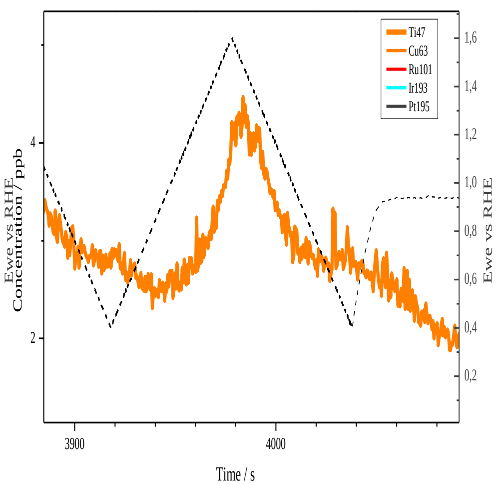










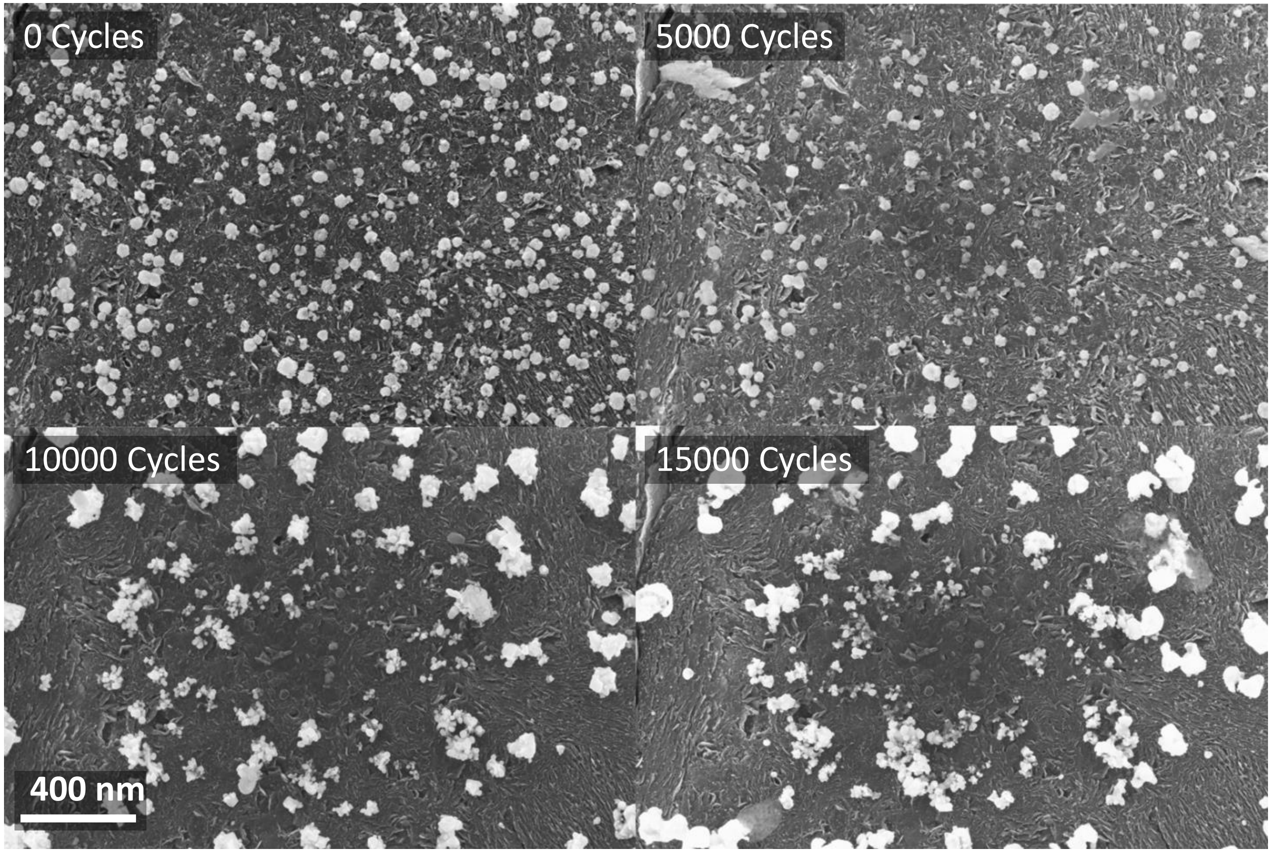


Tnx Leonard

unpublished

What about degradation at reductive potentials?

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

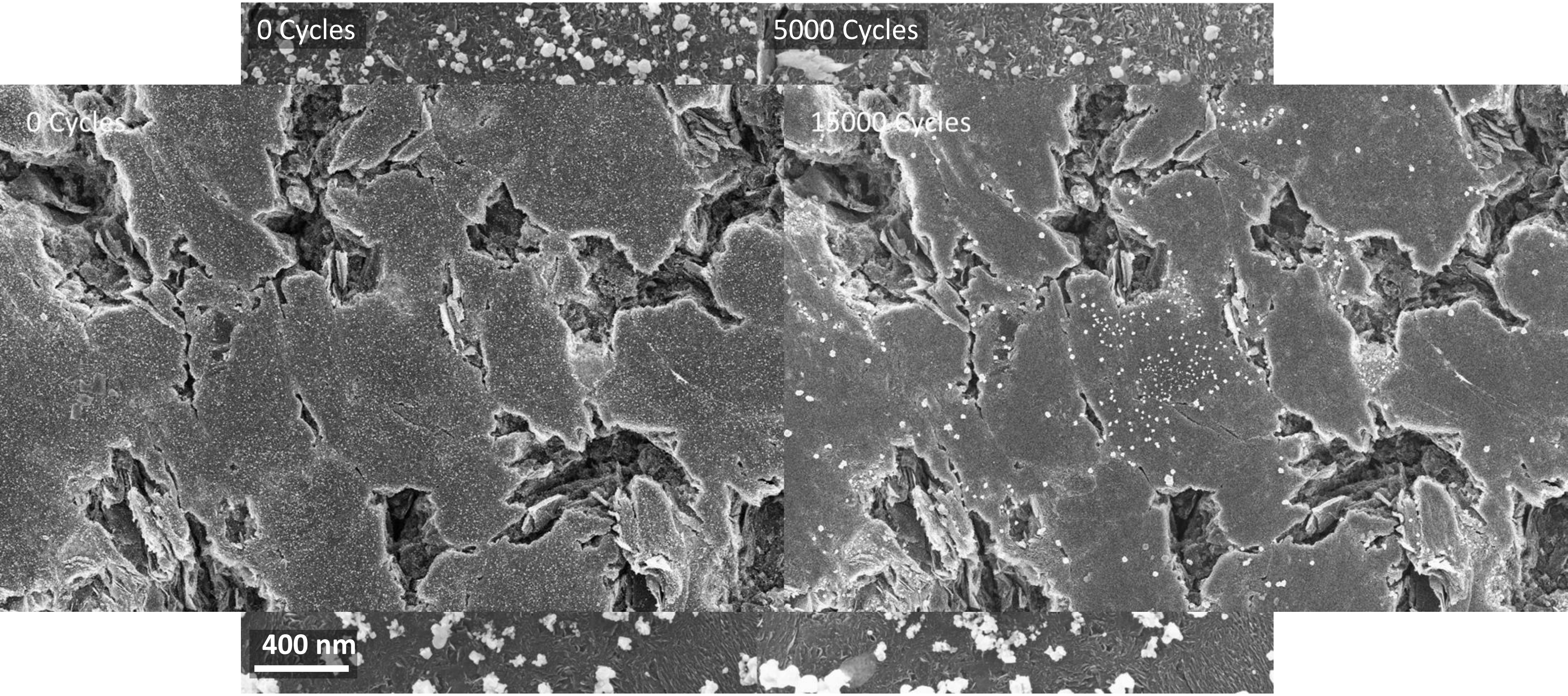


Vanrenterghrm, Hodnik, Applied Catalysis B: Environmental, 2018, 226, pp 396–402.

NEJC HODNIK

What about degradation at reductive potentials?

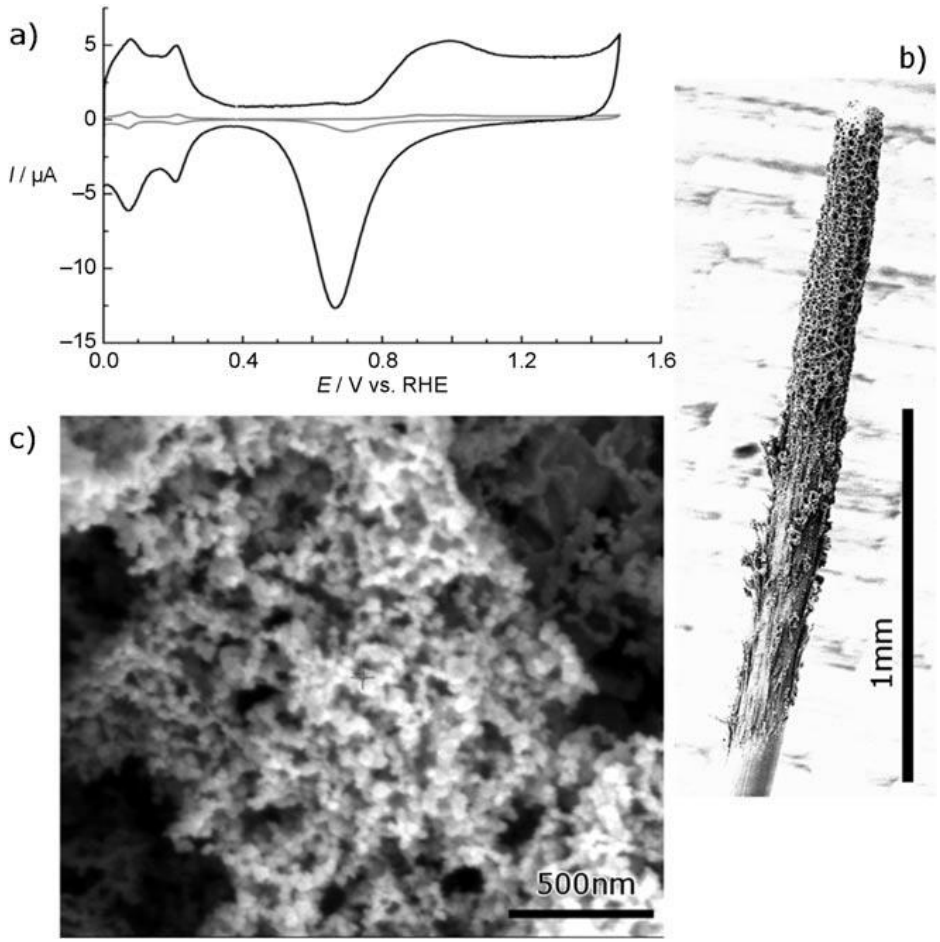
Degradatoion Ag via coalesence: 0, 5000, 10000, 15000 cycles



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

There is something else occurring at negative potentials!

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



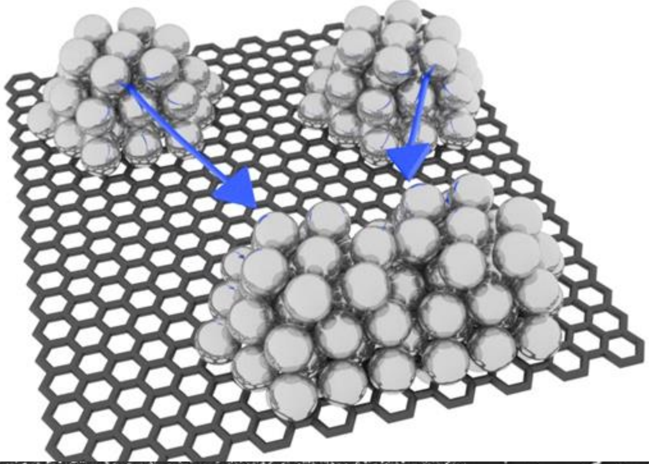
Cyclic voltammogram of a Pt wire 135 mm in diameter, submerged by 1 mm in 0.5m H2SO4 before (gray) and after (black) the wire was held for 1000 s at a dc of 10 V (7.2 V vs. HgO) in 10m NaOH. Graphite is used as anode to rule out the formation of interfering species by anodic dissolution. Sweep rate: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

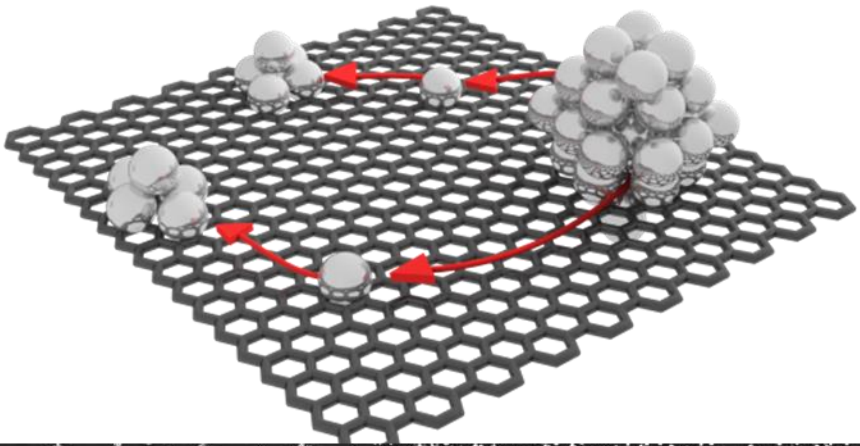
Angew. Chem. Int. Ed. 2011, 50, 6346 –6350

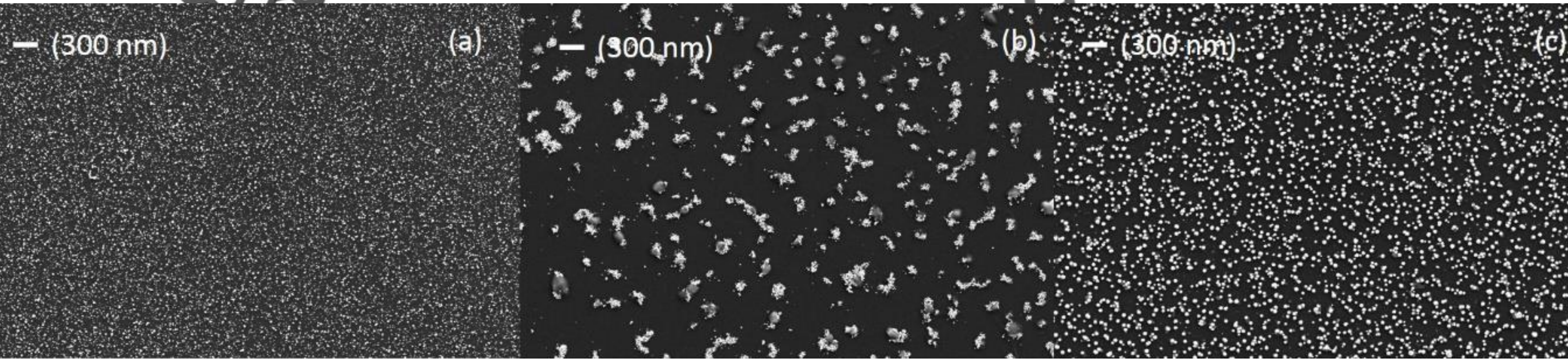
What about degradation at reductive potentials?

Electrochemical induced metal nanoparticle Coalescence / Dispersion

Interplay between Potential induced Coalesence vs. Dispersion





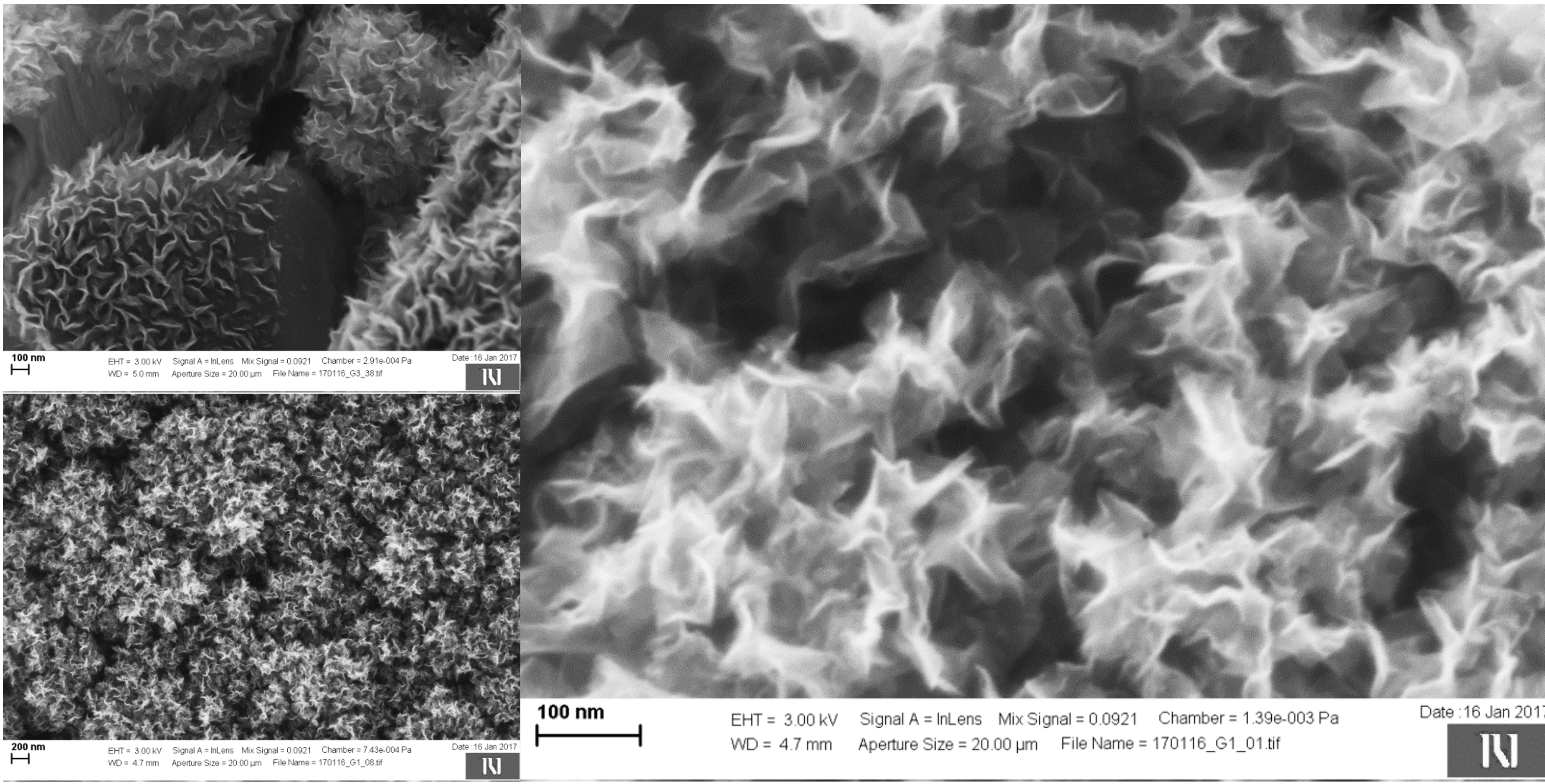


Vanrenterghrm, Hodnik, Applied Catalysis B: Environmental, 2018, 226, pp 396–402.

NEJC HODNIK

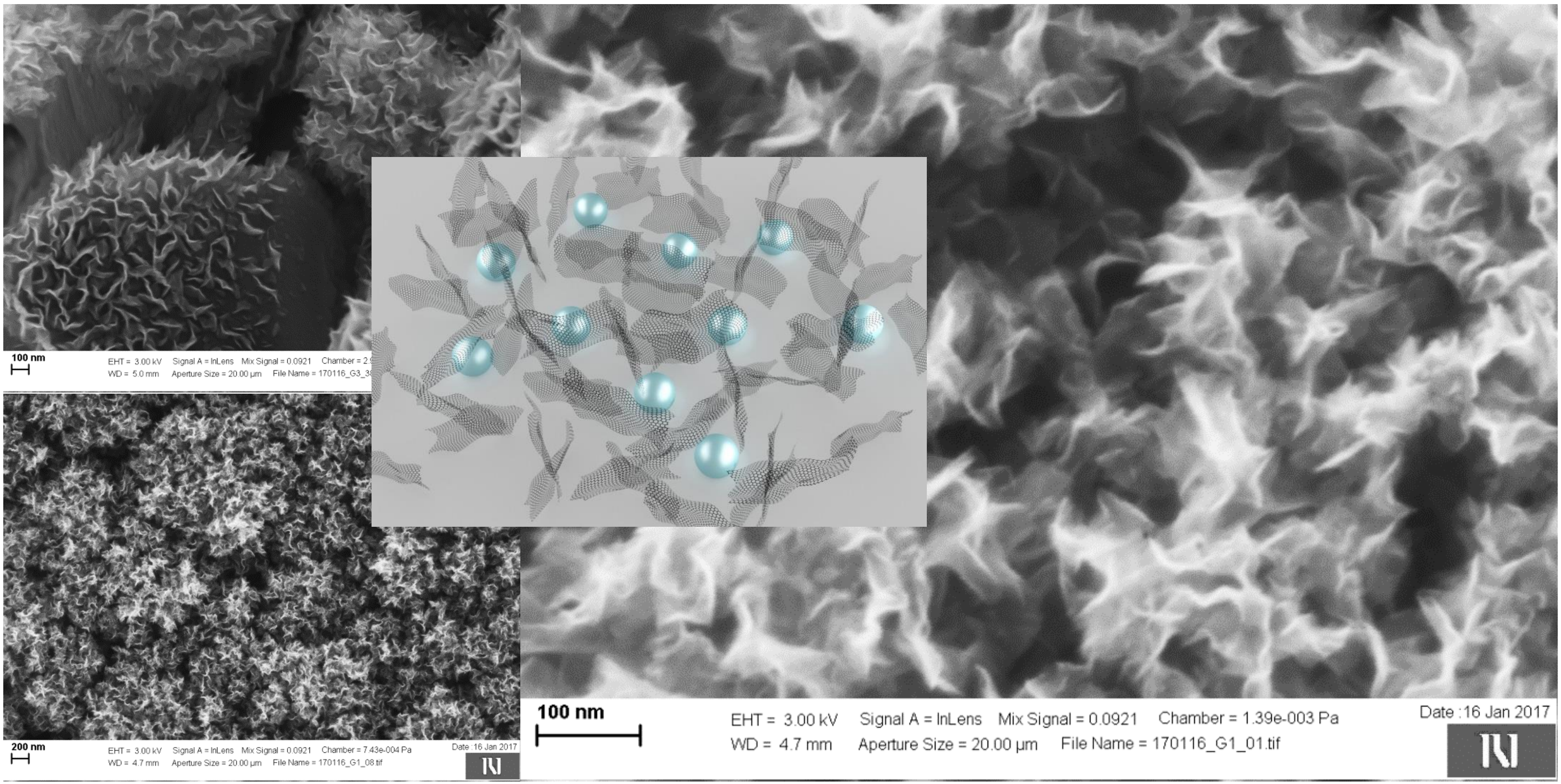
Forum40, Maj 2018, Ljubljana

Plasma Grown Vertically Aligned Graphene

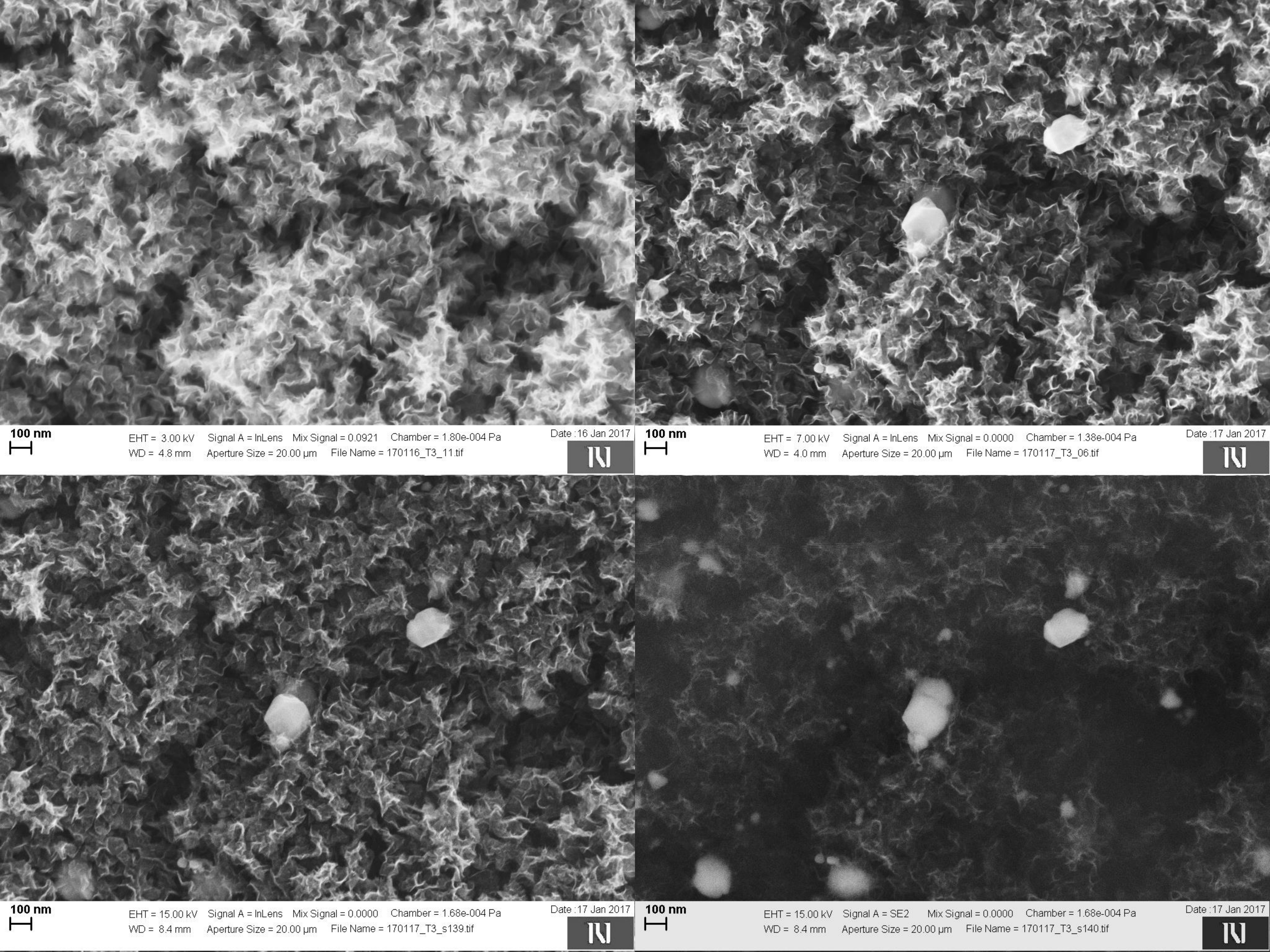


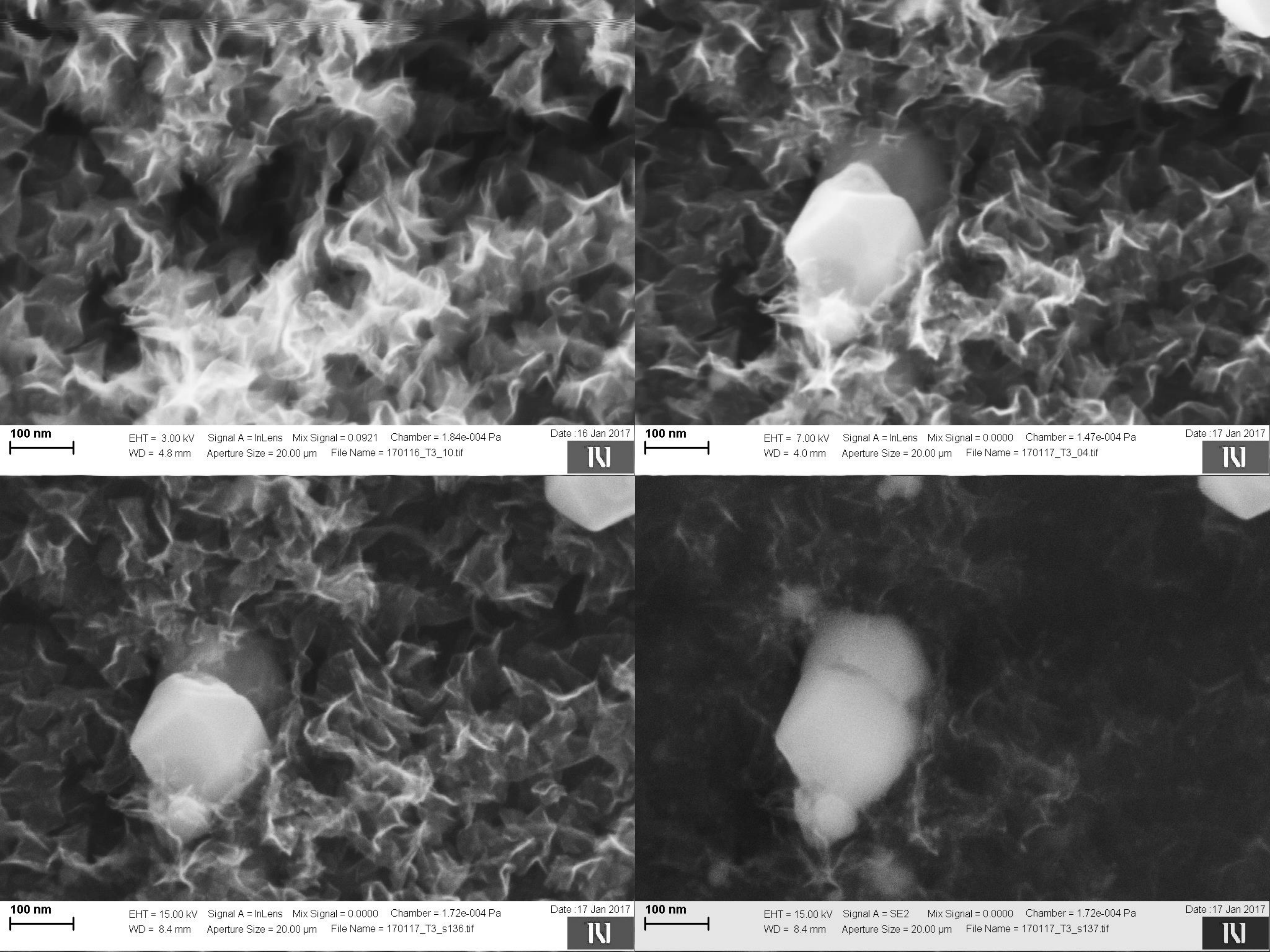
Vanrenterghrm, Hodnik, CHEMICAL COMMUNICATIONS, 2017,vol. 53, pp.9340-9343.

Plasma Grown Vertically Aligned Graphene



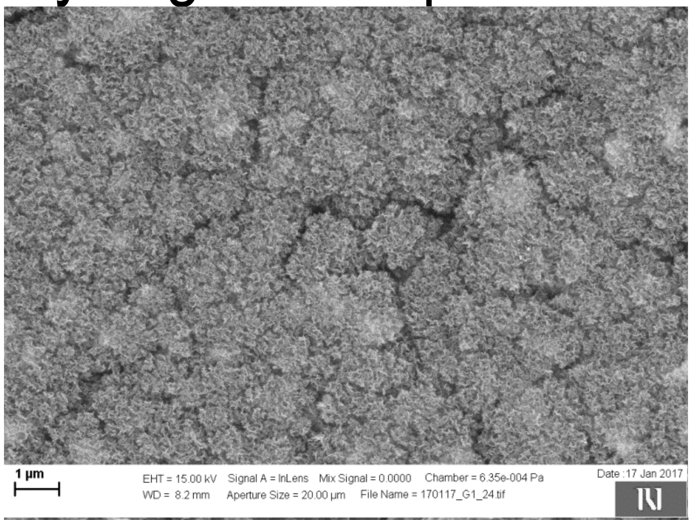
Vanrenterghrm, Hodnik, CHEMICAL COMMUNICATIONS, 2017,vol. 53, pp.9340-9343.

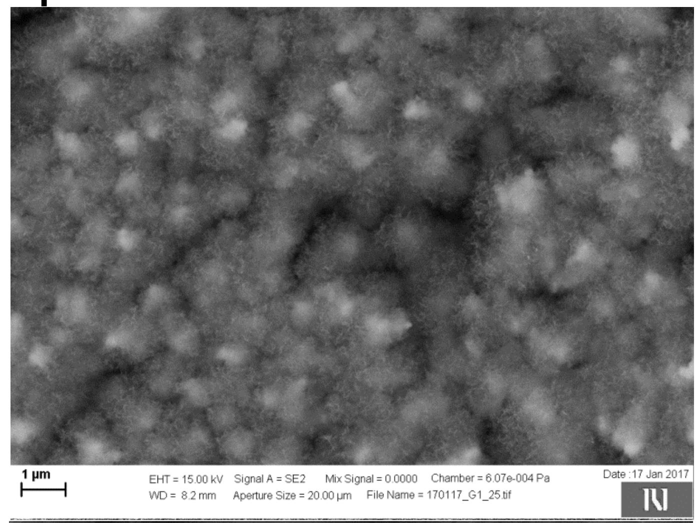

100 nm
EHT = 3.00 kV
Signal A = InLens
Mix Signal = 0.0921
Chamber = 1.80e-004 Pa
Date :16 Jan 2017
WD = 4.8 mm
Aperture Size = 20.00 µm
File Name = 170116_T3_11.tif
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0000
Chamber = 1.38e-004 Pa
Date :17 Jan 2017
WD = 4.0 mm
Aperture Size = 20.00 µm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


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

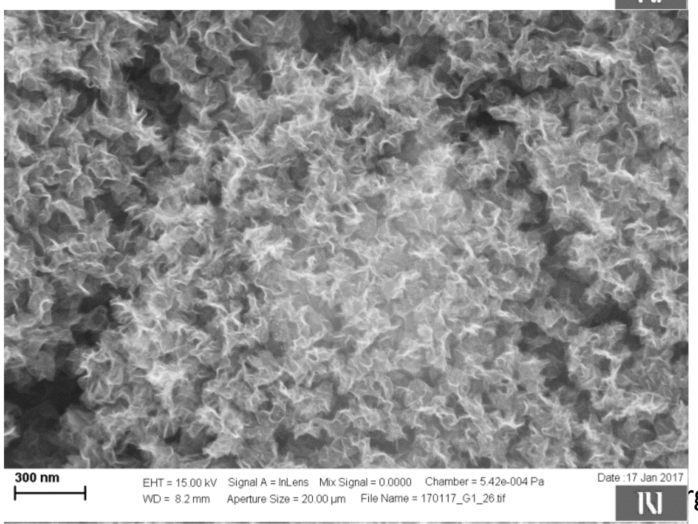
Increase of Electrodeposited Catalysts Stability via Plasma Grown Vertically Aligned Graphene Nanoparticles Movement Restriction!

in-lens detector

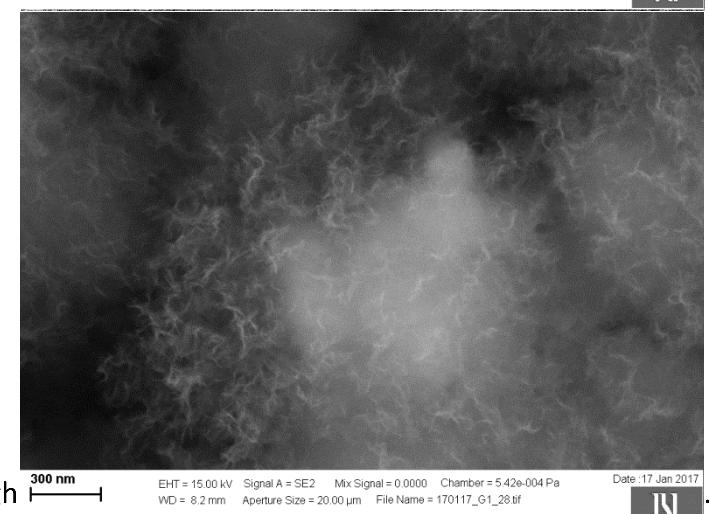




secondary electron detector

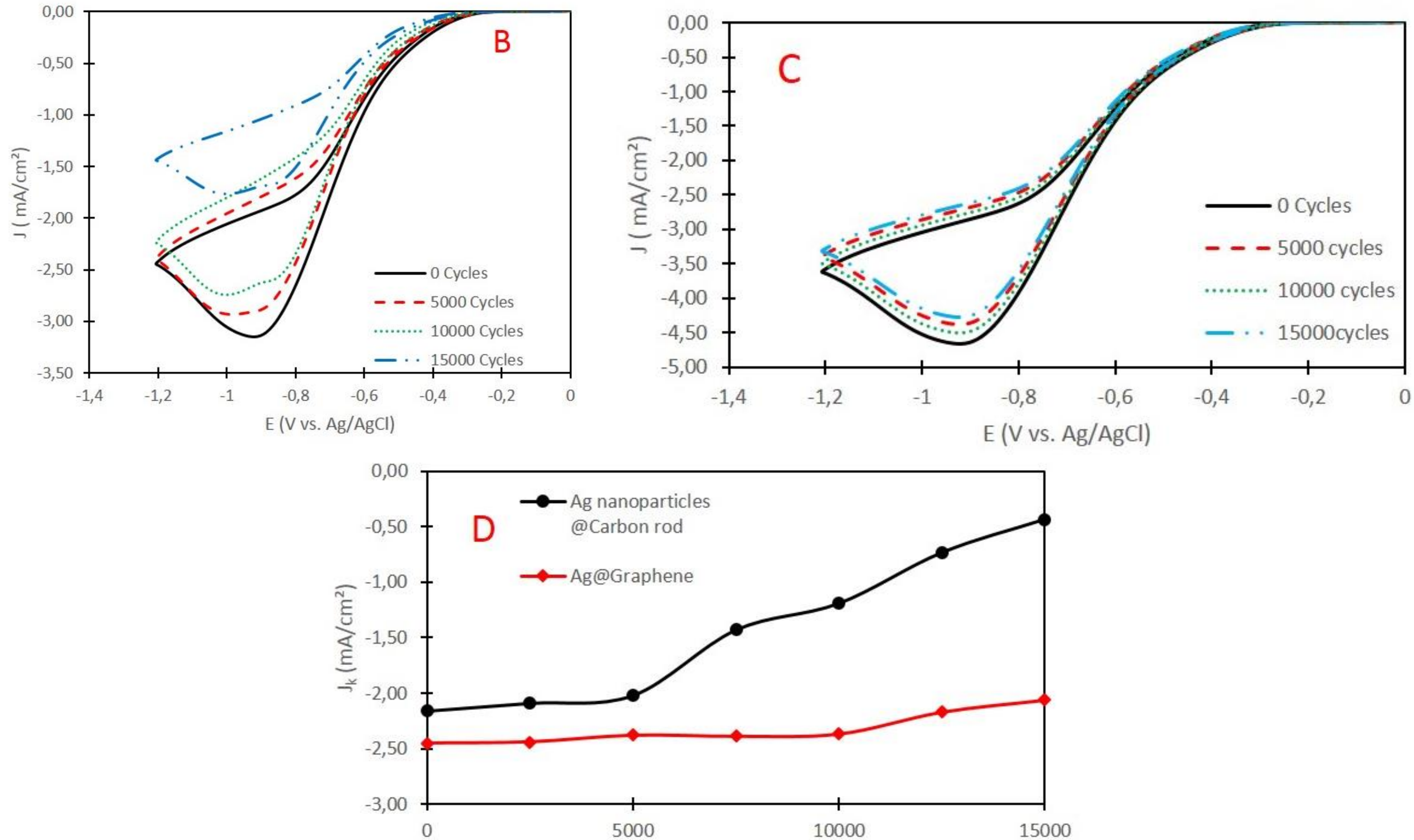


rgh



. 53, pp.9340-9343.

After electrochemical deposition



Vanrenterghrm, Hodnik, CHEMICAL COMMUNICATIONS, 2017,vol. 53, pp.9340-9343.

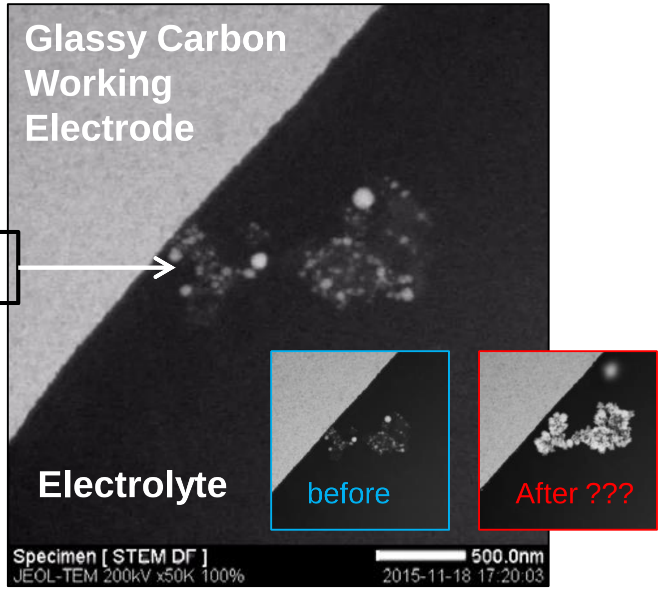
NEJC HODNIK

Forum40, Maj 2018, Ljubljana

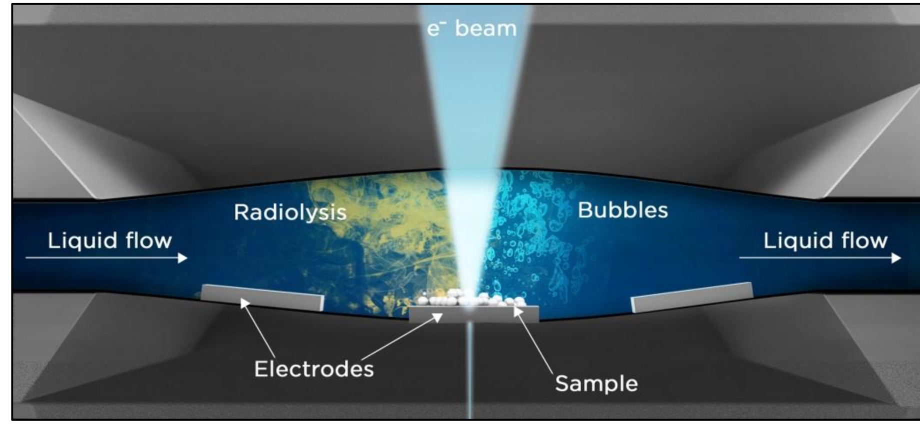
Electrochemical in-situ liquid TEM

time- and potential-resloved structural changes: Video!

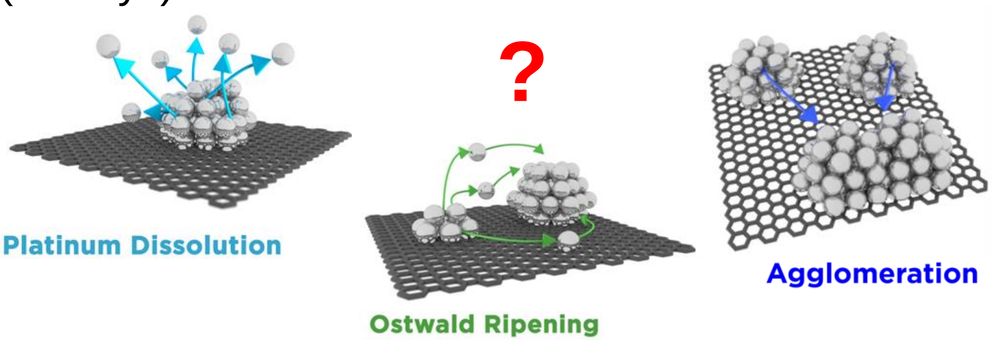
PtCu/C

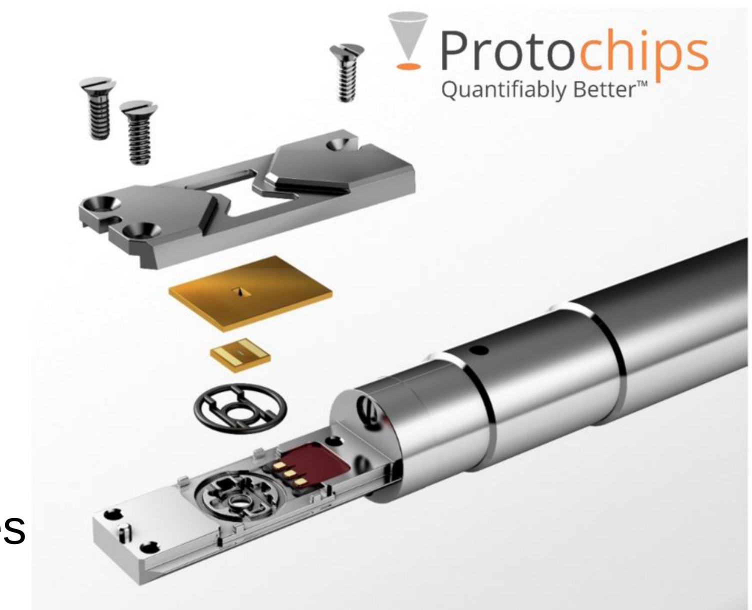


Agglomeration or deposition due to potential cycling (150 cyc) ?



Hodnik* et al. *Acc. Chem. Res.*, **2016**, *49* (9), pp 2015–2022





Most likely an artifact of electron beam!
To be sure it must be compared to IL-TEM that serves as a benchmark. In-situ liquid TEM needs IL-TEM!

Noble or Precious metals

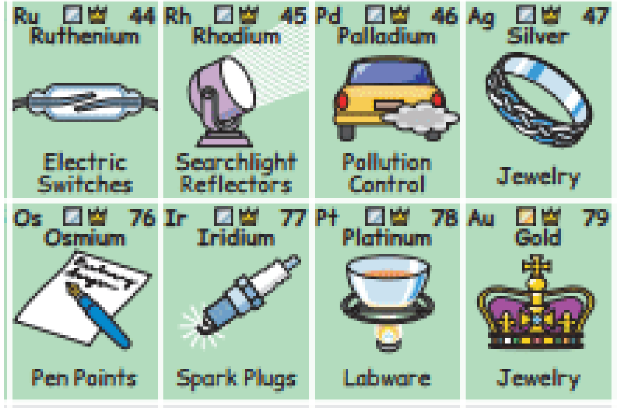
- Known from “4000 BC” and with a reach history since
- Useful due to unique functional properties: they are stable, resistant to oxidation, biocompatible and catalytically active

Till now 4230 tones of Pt was mined; now 200 tons annually

http://dillonmarsh.com/pgm01.html

Mostly used as:

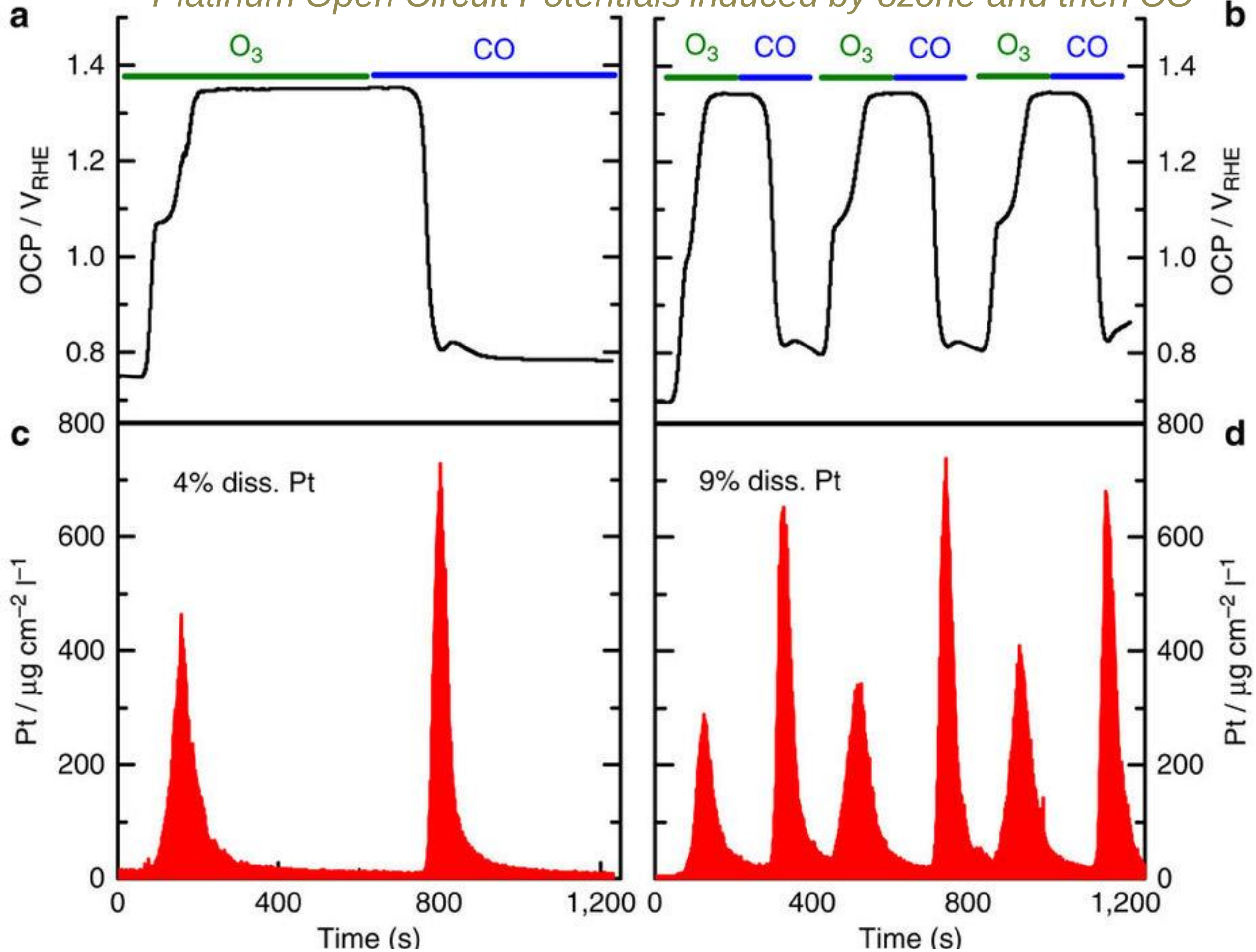
- Jewelry
- Electrical contacts
- (Electro)Catalysts



- In the future everything will be digitalized and free energy will come from sun
- Due to their price and scarceness we must break them down to nanoparticles – properties change; stability issues
- Perfect for el. microscopy and ICP-MS (high-z methodology approach)

- **recycling of PGM**

Platinum Open Circuit Potentials induced by ozone and then CO



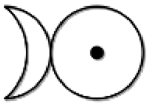
„transient dissolution“

Hodnik et al., *Nature Communications,* **2016,** 7, 13164 .

• recycling of PGM

Platinum Open Circuit Potentials induced by ozone and then CO

- We make use of Transient Dissolution phenomena

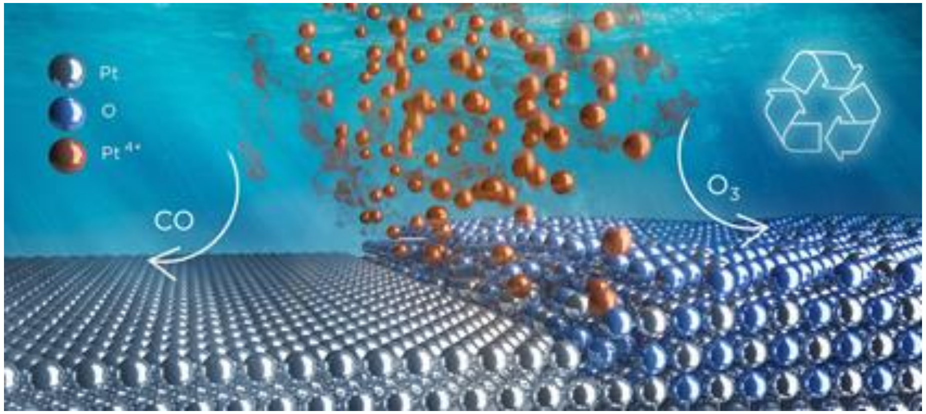


Compared to the State of the art: ***Aqua Regia*** **(alchemy)**

- *3:1 molar ratio of concentrated boiling nitric and hydrochloric acid*

My new patent pending process is:

- *Two orders of magnitude lower concentrated acids (c = 0.1 M, pH ~ 1)*
- *Room temperatures (20 °C)*
- *„No toxicity" (toxic gasses can be avoided)*
- *Environmentally and user Friendly (simple)*
- *Based on completely new chemistry (unpredicted by Pourbaix)*



Hodnik et al., *Nature Communications,* **2016,** 7, 13164 .

NEJC HODNIK

Platinum!

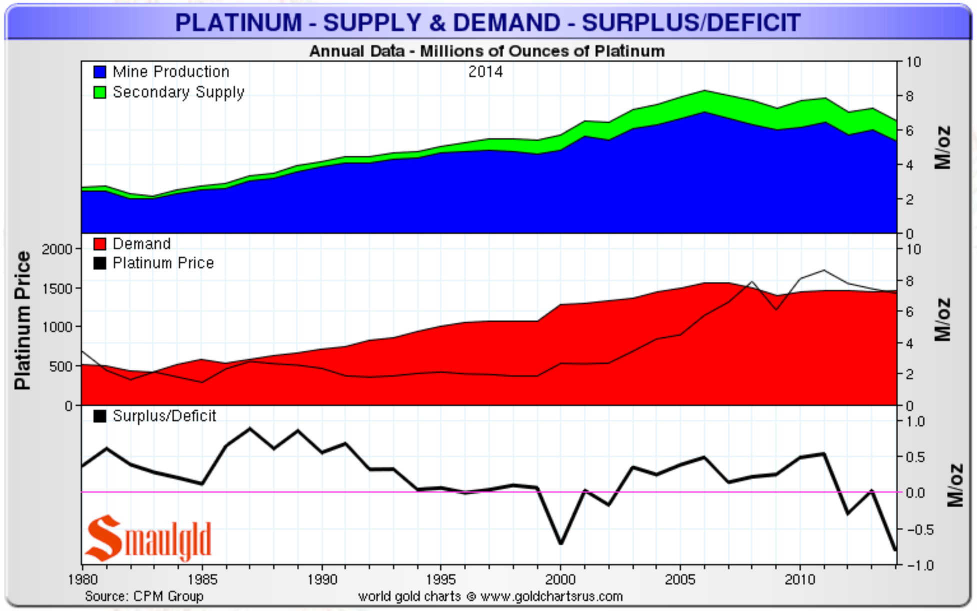
Important application areas for PGMs

Application area	Platinum group metal				
	Platinum	Palladium	Rhodium	Iridium	Ruthenium
Catalysts	✓	✓	✓	✓	✓
Electronics	✓	✓		✓	✓
Fuel cells	✓	✓	✓		✓
Glass, ceramics and pigments	✓		✓		
Medical/dental	✓	✓		✓	
Pharmaceuticals	✓	✓			✓
Photovoltaic					✓
Super-alloys					✓

Source: Recycling the Platinum Group Metals: A European Perspective

Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

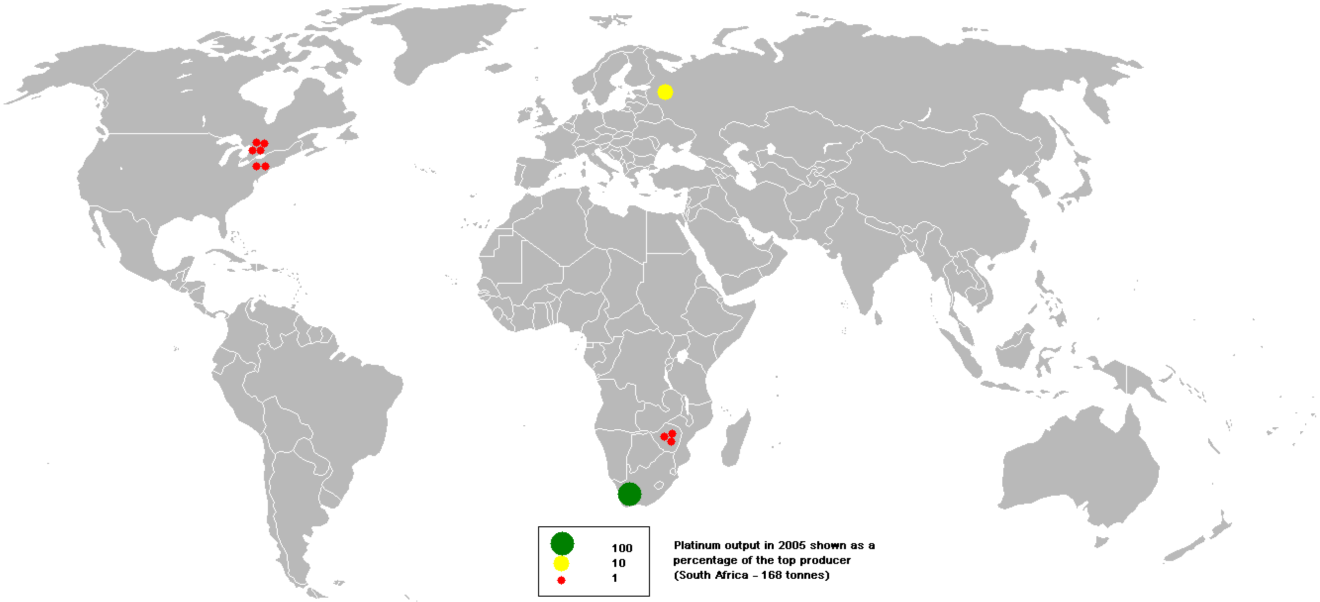
Platinum!



Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

Platinum!

For EU urban mining is the obvious way to minimalize import dependence from foreign countries.

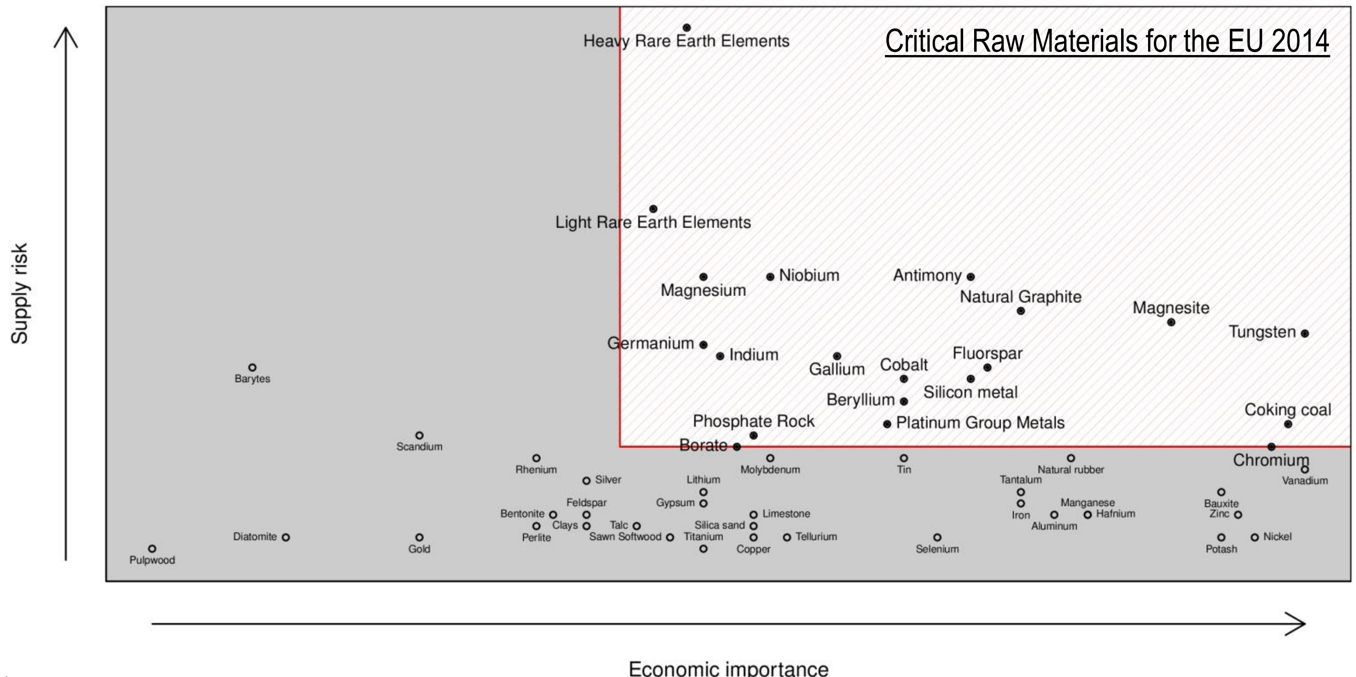


Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

NEJC HODNIK

Critical Raw Materials - CRMs

- EU makes a list of materials that are of supply risk to our well-being
- CRMs demand is increasing – High tech equipment like cell phones contain CRMs (also PGM)
- Solution – **Recycle** and not export to third world countries (environment and health problems)
- **Circular & Hydrogen Economy**



http://europa.eu/rapid/press-release_MEMO-14-377_en.htm

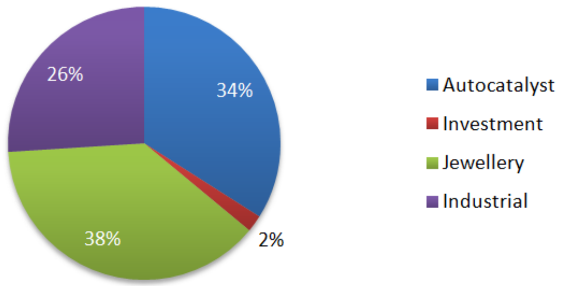
NEJC HODNIK

Forum40, Maj 2018, Ljubljana

"Till now 4230 tons of Pt was mined." – 6x6x6m cube

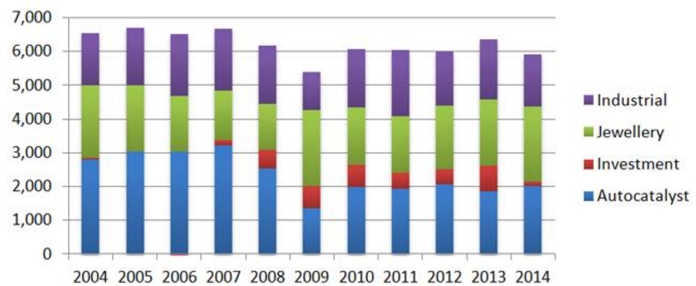
Platinum!

Platinum Net Demand By Application 2014 Total 184 tons net



Automotive Catalytic Converters
-Now

Platinum Demand By Application



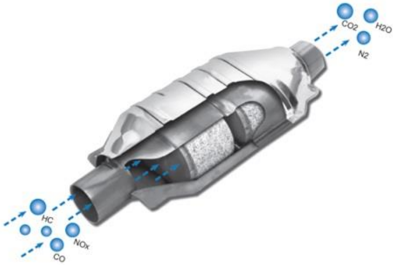
Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

NEJC HODNIK

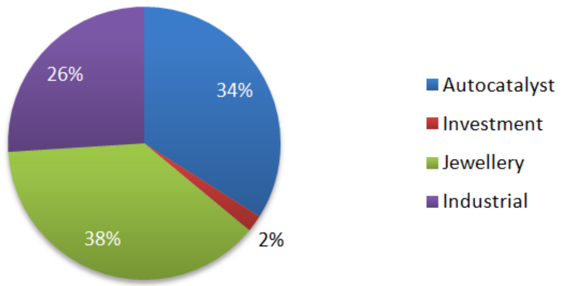
"Till now 4230 tons of Pt was mined." – 6x6x6m cube

Platinum!

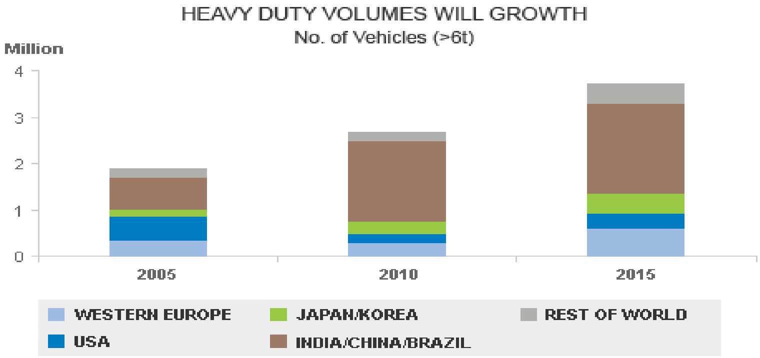
Automotive Catalytic Converters
-Now



Platinum Net Demand By Application 2014 Total 184 tons net



Platinum Demand By Application



Source: Johnson Matthey, JD Power and IHS Automotive[1], 2011

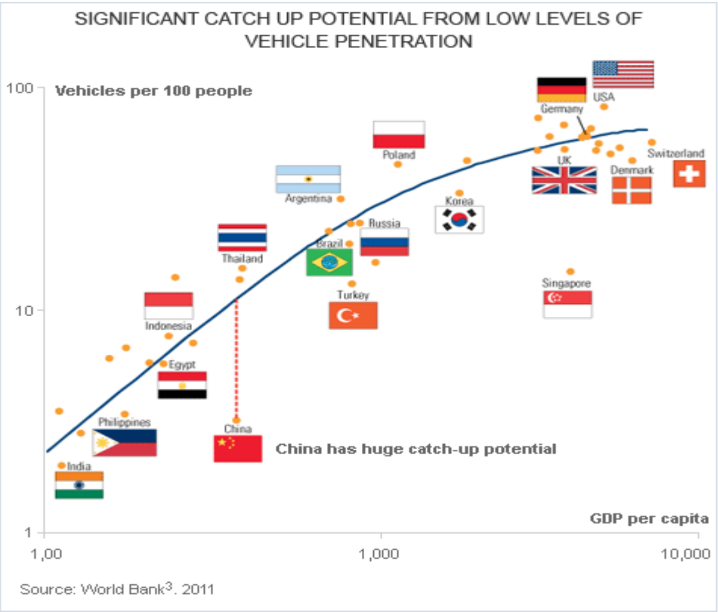
Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

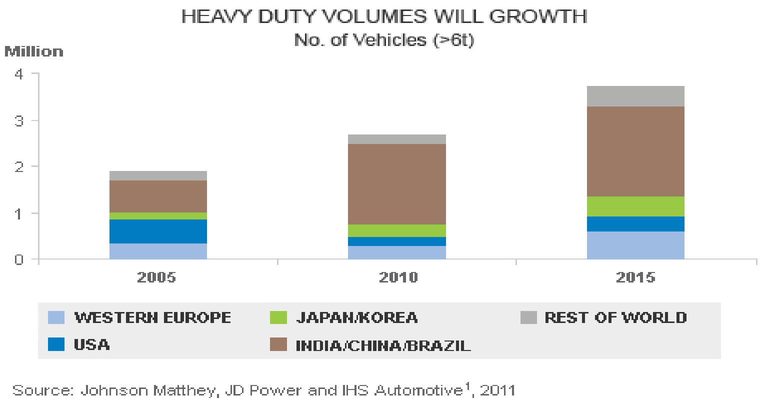
NEJC HODNIK

Forum40, Maj 2018, Ljubljana

“Till now 4230 tons of Pt was mined.” – 6x6x6m cube

Platinum!





Automotive Catalytic Converters
-Now

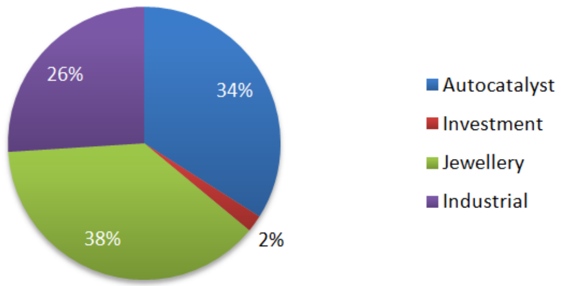
Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

NEJC HODNIK

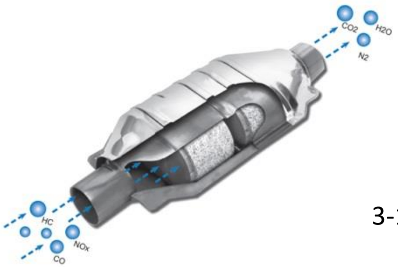
“Till now 4230 tons of Pt was mined.” – 6x6x6m cube

Platinum!

Platinum Net Demand By Application 2014 Total 184 tons net

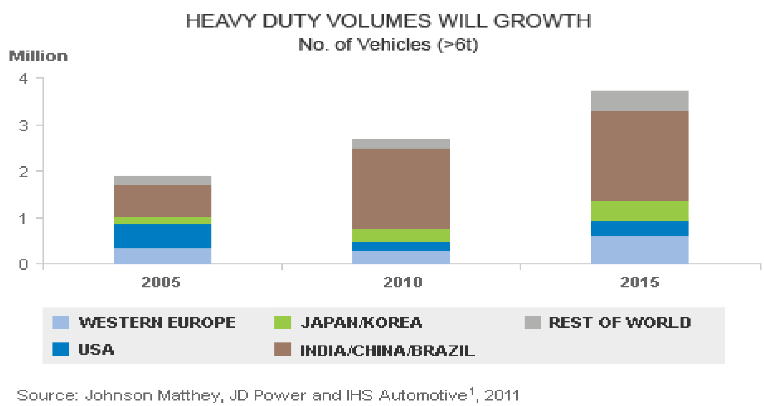


Automotive Catalytic Converters
-Now

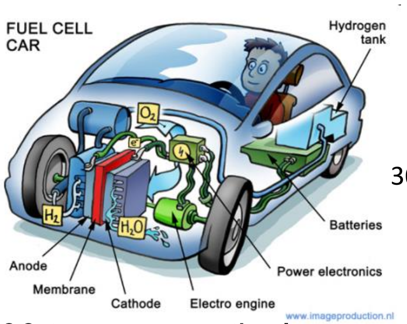


3-15 g of Pt

Platinum Demand By Application



Fuel Cell Cars
-Future



30-40 g of Pt

- Proven resources: 30,000 tons respectively.
- Annual production: 200 tons respectively (10% recycle).
- Reserves: in the range of 100 years.

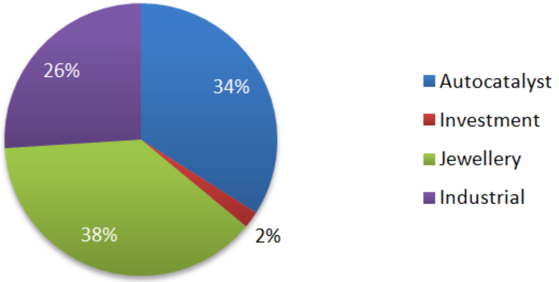
Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

NEJC HODNIK

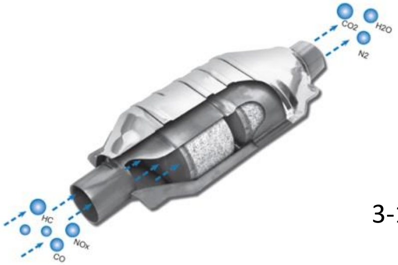
"Till now 4230 tons of Pt was mined." – 6x6x6m cube

Platinum!

Platinum Net Demand By Application 2014 Total 184 tons net

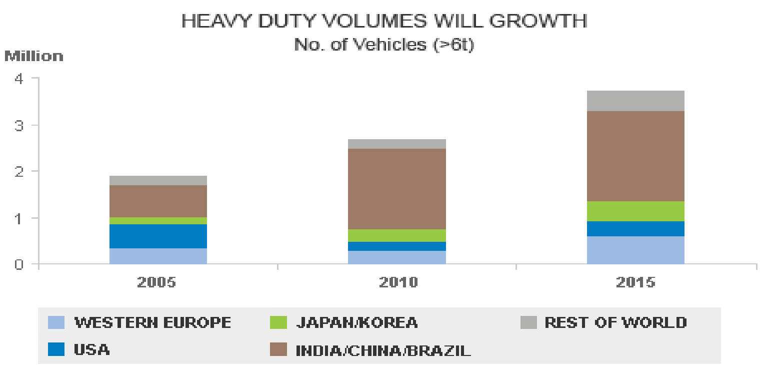


Automotive Catalytic Converters
-Now



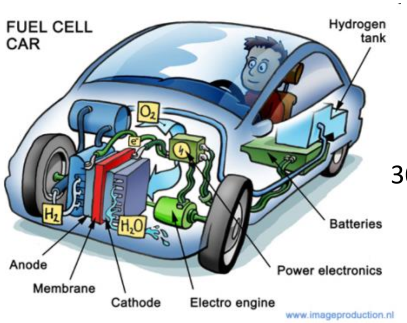
3-15 g of Pt

Platinum Demand By Application



Source: Johnson Matthey, JD Power and IHS Automotive[1], 2011

Fuel Cell Cars
-Future



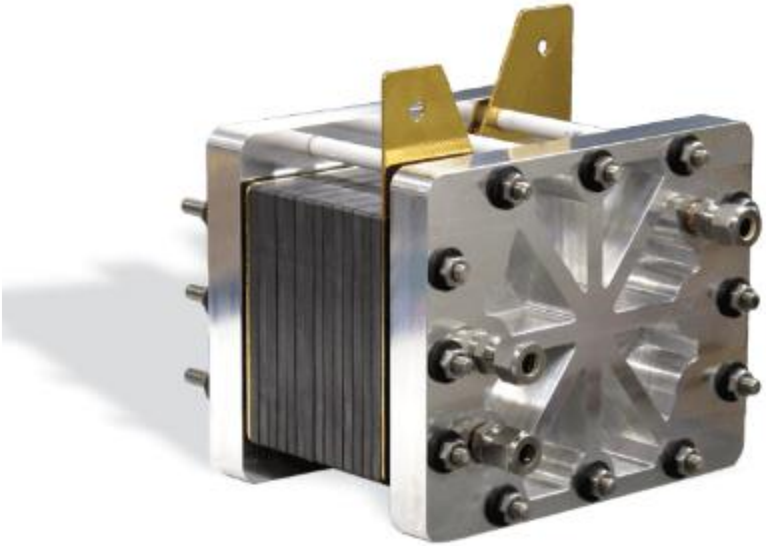
30-40 g of Pt

Mining Ores
-not in EU

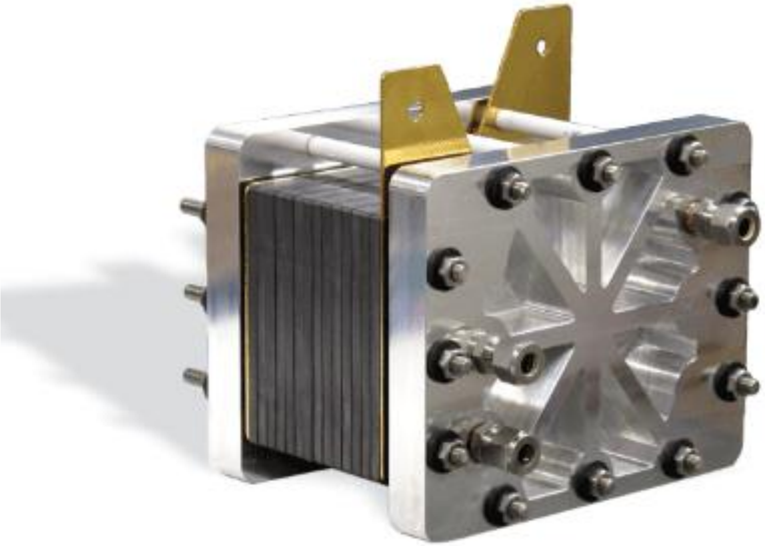
Source: http://en.wikipedia.org/wiki/Platinum; https://smaulgld.com/platinum-supply-and-demand, http://www.canplats.ca/html/Investor_Information/Platinum_Market/index.cfm, www.platinuminvestment.com

- **recycling of PGM**

→



- **recycling of PGM**



5 g

5 g ?

High Value Asteroid Materials

ASTEROID ELEMENTAL ABUNDANCE RELATIVE TO EARTH'S CRUST

H Hydrogen	17x
C Carbon	75x
N Nitrogen	74x
O Oxygen	1x
Fe Iron	4x
Co Cobalt	27x
Ni Nickel	155x
Ru Ruthenium	810x
Rh Rhodium	180x
Pd Palladium	44x
Os Osmium	440x
Ir Iridium	540x
Pt Platinum	196x

VOLATILES AND H_2O
to fuel the growth of humanity into new frontiers

Potable Water
Radiation Shielding

Fuel

Refrigerant

Agriculture
Metallurgy

INDUSTRIAL METALS
to construct and sustainably service space platforms

PLATINUM GROUP METALS
to support demand growth on Earth

Catalytic Converters

LCDs

Advanced materials

Cancer treatments

Despite desire to reduce dependency, <u>one-in-four</u> manufactured goods require PGMs.

PLANETARY RESOURCES

High V
als
ASTEROID ELEMENTAL ABU
17x
H
Hydrogen
75x
C
Carbon
74x
N
Nitrogen
4x
Fe
Iron
27x
Co
Cobalt
810x
Ru
Ruthenium
180x
Rh
Rhodium
440x
Os
Osmium
540x
Ir
Iridium
PLANETARY
RESOURCES
KNIGHT FRANK
ASTEROID INDEX
THE WEALTH REPORT 2014
Knight Frank
ASTERIODS TO WATCH
Near-earth objects (including their main minerals) that will make an approach to Earth of less than 0.2AU*, travelling at less than 8km/s.
NEXT APPROACH OCTOBER 2017 / 0.1563 DISTANCE FROM EARTH (AU)***
JULY 2017 / 0.121 (AU)***
MARCH 2017 / 0.192 (AU)***
JANUARY 2016 / 0.103 (AU)***
FEBRUARY 2015 / 0.064 (AU)***
JANUARY 2015 / 0.0833 (AU)***
JANUARY 2014 / 0.149 (AU)***
1989 UQ
IRON, HYDROGEN, AMMONIA, NITROGEN
APPROX VALUE (US$)** $13 trillion
$2 trillion ESTIMATED PROFIT (US$)**
2000 CE59
MAGNESIUM SILICATE ALUMINIUM IRON SILICATE
APPROX VALUE (US$)** $5 trillion
$923 billion ESTIMATED PROFIT (US$)**
2000 BM19
PLATINUM, NICKEL, IRON
APPROX VALUE (US$)** $36 trillion
$3 trillion ESTIMATED PROFIT (US$)**
2000 AC6
NICKEL, IRON
APPROX VALUE (US$)** $2 billion
$247 million ESTIMATED PROFIT (US$)**
1999 JV6
NICKEL, IRON, COBALT
APPROX VALUE (US$)** $1.5 trillion
$218 billion ESTIMATED PROFIT (US$)**
The Wealth Report 2014 highlights the rising trend for private wealth investment in space research — from asteroid mining to sub-orbital space travel. Knight Frank has identified more than 70 wealthy individuals, with a combined wealth of over US$200 billion, who are targeting this sector and the potentially huge rewards that, as our graphic shows, could be on offer. To find out how this investment is even set to transform earth-based property markets go to KnightFrank.com/WealthReport
* 1AU or Astronomical unit is equivalent to 93 million miles
** Source: Asterank, http://www.asterank.com/ 14 Jan 2014 Value estimates are based on the mass of a given asteroid and its spectral type. Asteroid spectra is used to infer composition, which, in conjunction with current market prices, determine potential value.
*** Source: NASA http://neo.jpl.nasa.gov/ca/
KnightFrank.com/WealthReport
S AND H2O
growth of
nto new frontiers
AL METALS
t and
service space
GROUP METALS
demand growth on
dependency,
d goods require PGMs.

WEEE is a big environmental and health problem in developing countries!

- e-waste disposal is still not controlled; 75% ends up illegally in developing countries. – Huge business and Huge problem!
- Only 12.5% of global e-waste is recycled where issues are that recycling is difficult, dangerous, expensive and toxic. Developing countries are dumping sites for e-waste.
- Noble metals demand will only increase in the future!

NEJC HODNIK

Forum40, Maj 2018, Ljubljana

WEEE is a big environmental and health problem

- e- … es.
  –
- O … t,
  da … ste.
- N

COMMENT

ECONOMICS Joseph Stiglitz's guide to the failures of eurozone policymakers p.26

DEVELOPMENT Parenting tips from the lab of a 'Berkley bubbe' p.27

CHINA A bold and epic portrait of a civilization shaped by water p.28

CAPACITY-BUILDING Mentoring scheme supports female scientists in Cameroon p.30

JIEZHAO/CORBIS/GETTY

An electronic-waste recycling factory in Hubei, China.

Take responsibility for electronic-waste disposal

International cooperation is needed to stop developed nations simply offloading defunct electronics on developing countries, argue **Zhaohua Wang, Bin Zhang** and **Dabo Guan**.

The world is producing ever more electrical and electronic waste. The quantity of dumped computers, telephones, televisions and appliances doubled between 2009 and 2014, to 42 million tonnes per year globally[1,2].

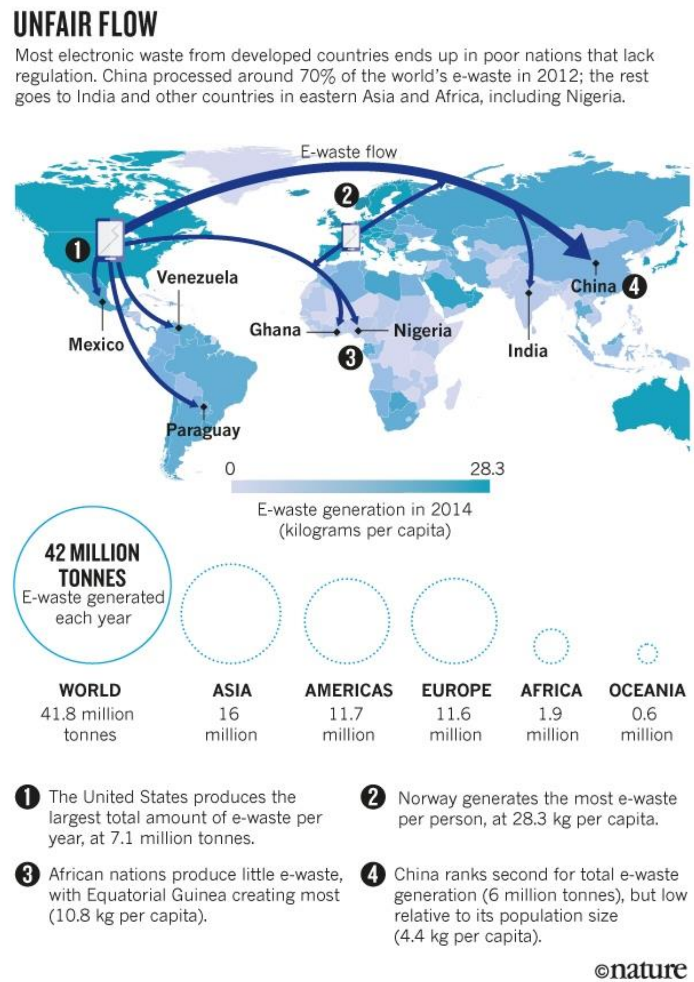
Developed countries, especially in North America and Europe, produce the most e-waste (see 'Unfair flow'). The United States generates the largest amount, and China the second most[3].

Much of this waste ends up in the developing world, where regulation is lax. China processed about 70% of the world's e-waste in 2012[4]; the rest goes to India and other countries in eastern Asia and Africa, including Nigeria[5]. Non-toxic components — such as iron, steel, copper and gold — are valuable, so are more frequently recycled than toxic ones[4]. Disposal plants release toxic materials, volatile organic chemicals and heavy metals, which can harm the environment and human health.

Lead levels sampled in the blood ▶

4 AUGUST 2016 | VOL 536 | NATURE | 23

© 2016 Macmillan Publishers Limited, part of Springer Nature. All rights reserved.



NEJC HODNIK

Forum40, Maj 2018, Ljubljana

WEEE is a big environmental and health problem


COMMENT

ECONOMICS Joseph Stiglitz's guide to the failures of

DEVELOPMENT Parenting tips from the lab of a

CHINA A bold and epic portrait of a civilization shaped by

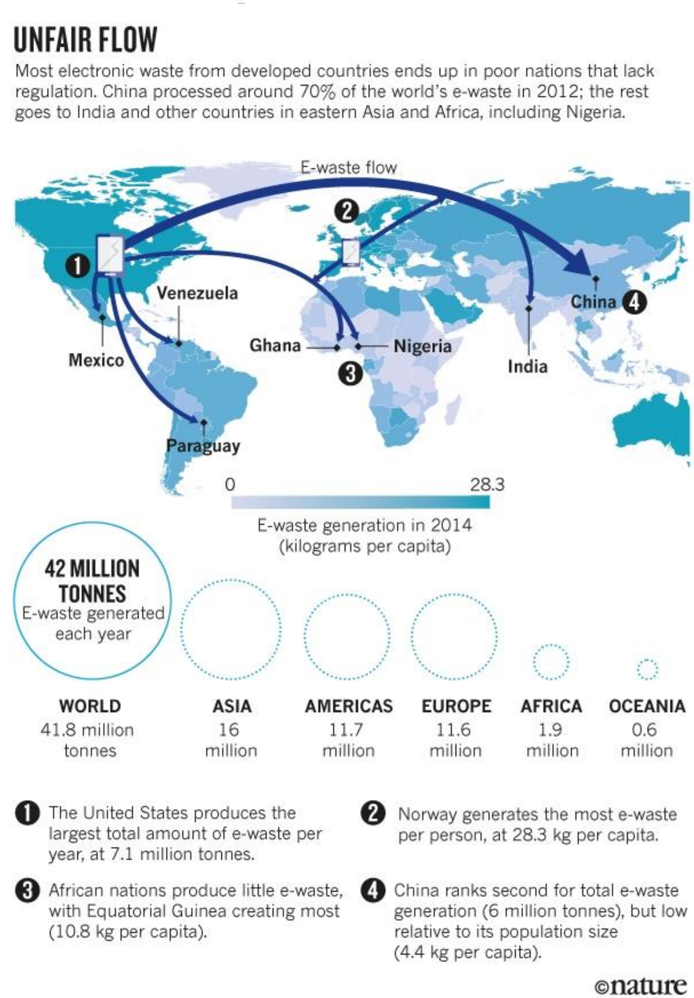
CAPACITY-BUILDING Mentoring scheme supports female

- e-

es.

t,

ste.

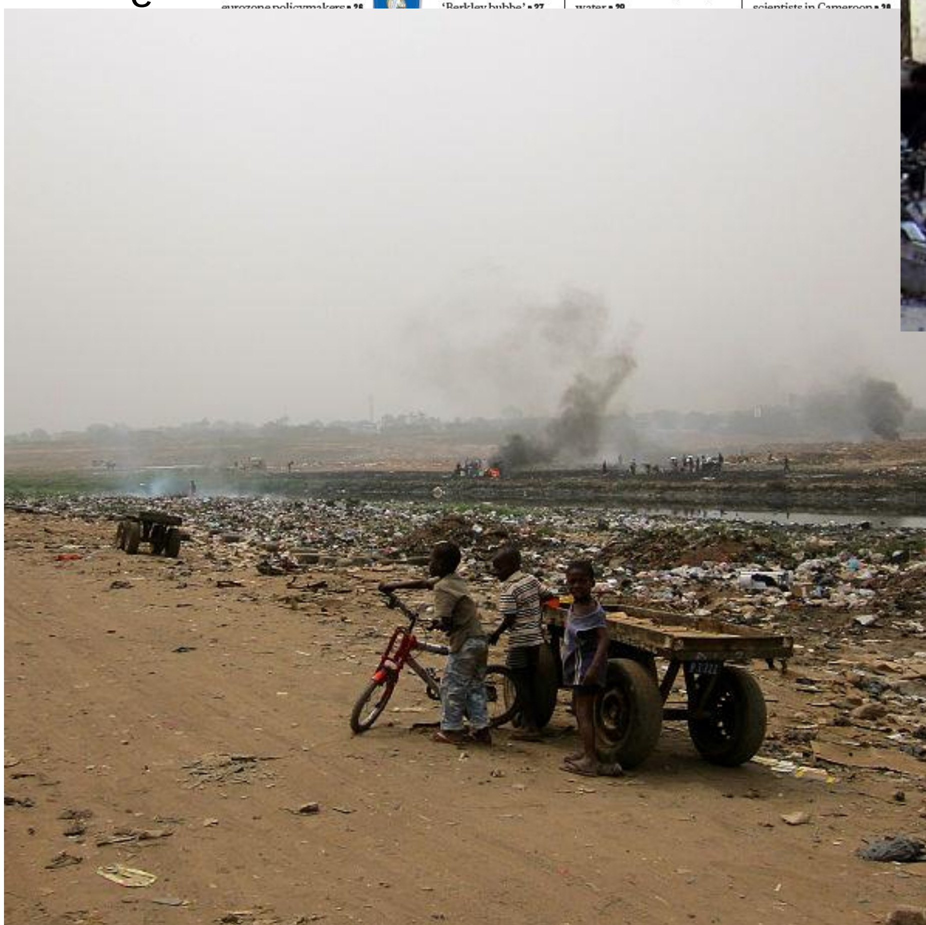


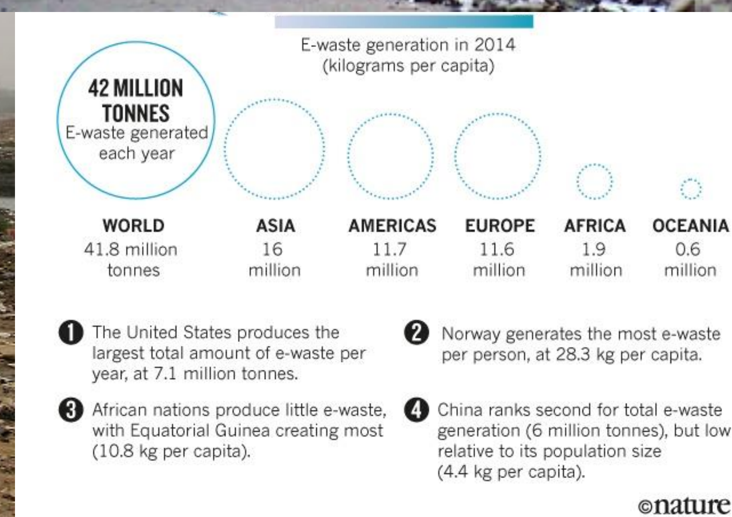
NEJC HODNIK

Forum40, Maj 2018, Ljubljana

WEEE is a big environmental and health problem

- e-





NEJC HODNIK

WEEE is a big environmental and health problem

COMMENT

ECONOMICS Joseph Stiglitz's guide to the failures of

DEVELOPMENT Parenting tips from the lab of a

CHINA A bold and epic portrait of a civilization shaped by

CAPACITY-BUILDING Mentoring scheme supports female

- e-

http://www.networkworld.com/ http://www.fokusz.info/

http://www.networkworld.com/ http://www.fokusz.info/

WEEE is a big environmental and health problem

http://www.networkworld.com/ http://www.fokusz.info/

http://www.networkworld.com/ http://www.fokusz.info/

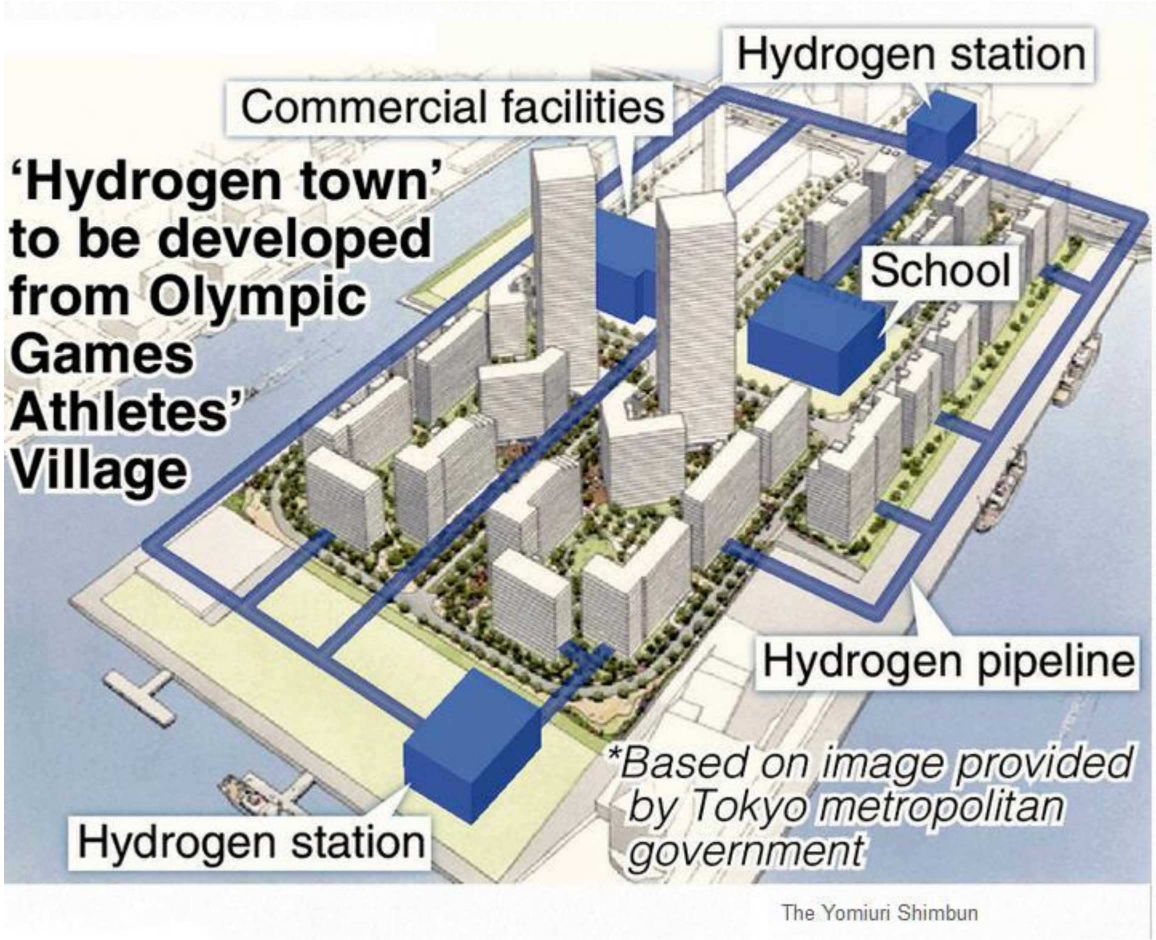
NEJC HODNIK

2020 Japan Olympics

“Tokyo 2020 medals could be made of electronic trash: Olympic organizers look to 'urban mine' of e-waste to find gold and silver.”

2020 Japan Olympics

“Japan is planning to turn the athletes' village for the 2020 Olympics in Tokyo into a "hydrogen town", where electricity and hot water are generated from hydrogen.”



Thank you for your attention!

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

Forum40, Maj 2018, Ljubljana