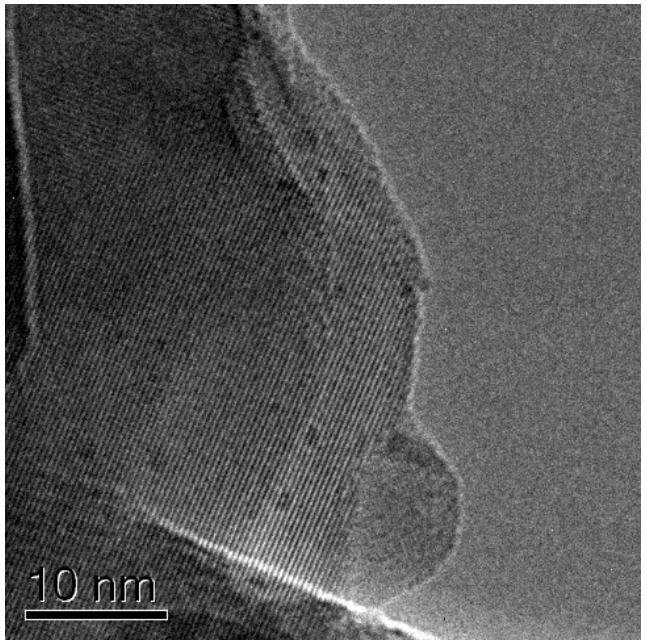
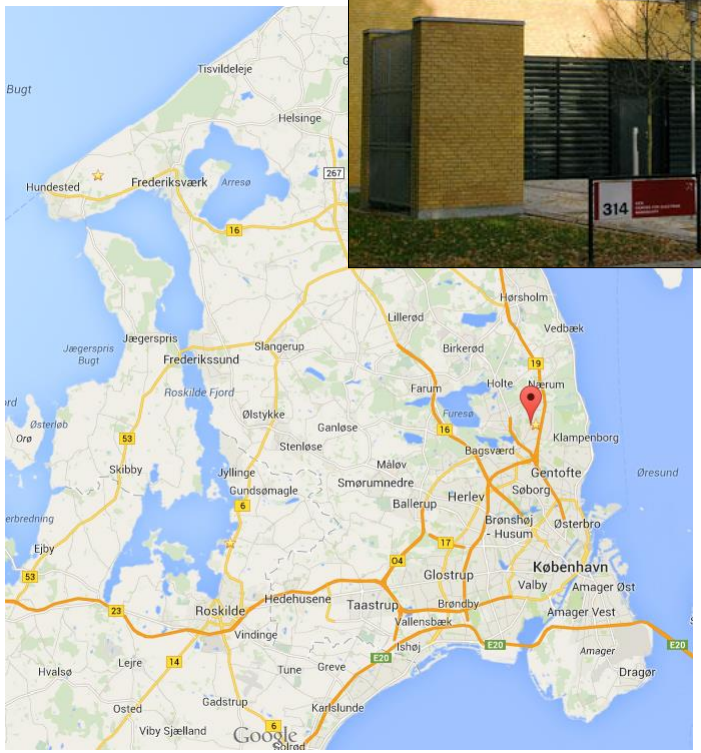
Environmental TEM: Principle, Limitation and Application

Jakob B. Wagner





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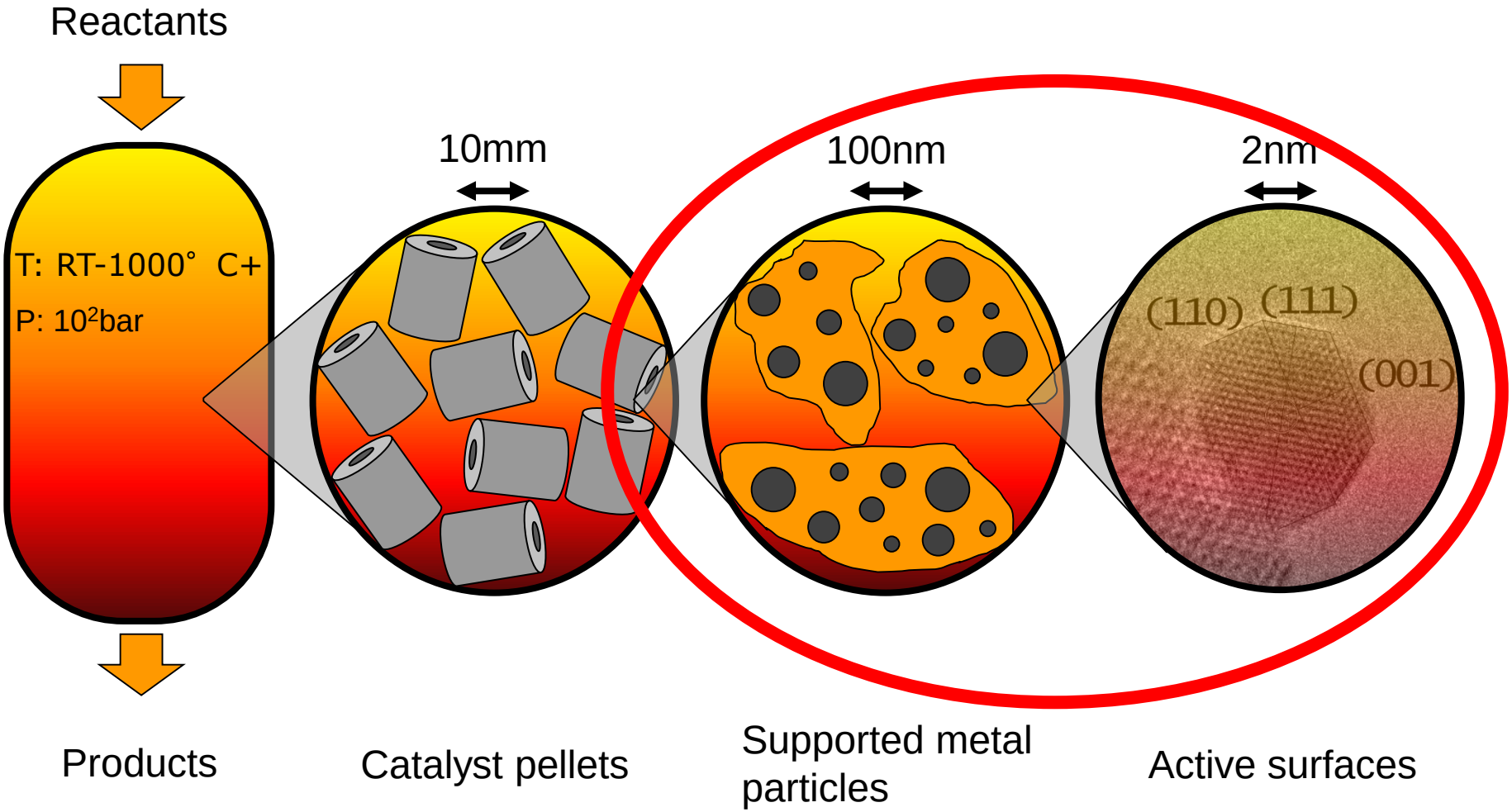
A Look Inside the Reactor



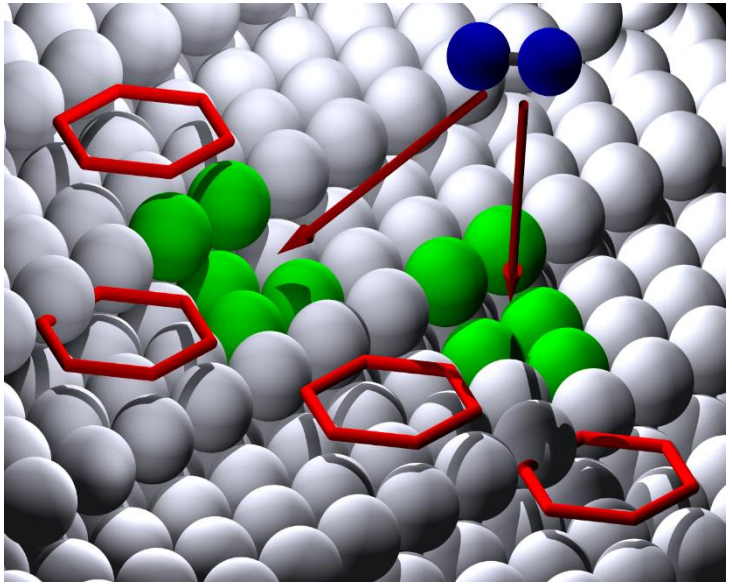
What is *In Situ* Microscopy

- Depends on who you ask!
- Observations of materials' dynamic response to an externally applied stimulus in the microscope

Does the light stay on…

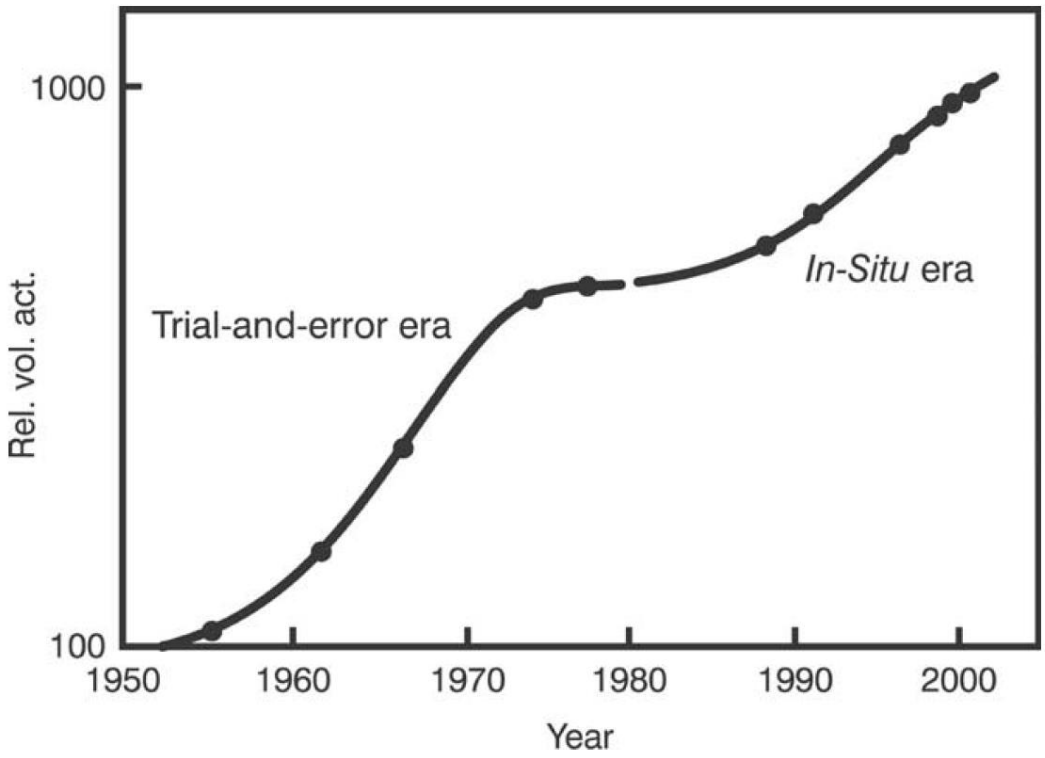
Why do We Want to do *In Situ* Microscopy?

- Conventional electron microscopy does not always tell the full story
  - Samples are (usually) not in their operational environment
- Materials respond dynamically to changes in environment
  - Surface reconstruction due to gas adsorption
  - Phase transitions
  - Growth
- Essential for establishing structure-activity correlations



b_5 sites on the (105) surface of Ru. These sites were proposed to be the active sites for N_2 splitting (van Hardeveld and von Montfoort Surf. Sci 4 (1966) 396. Figure adapted from T. W. Hansen *et al.* Catal. Lett. 84 (2002) 7.

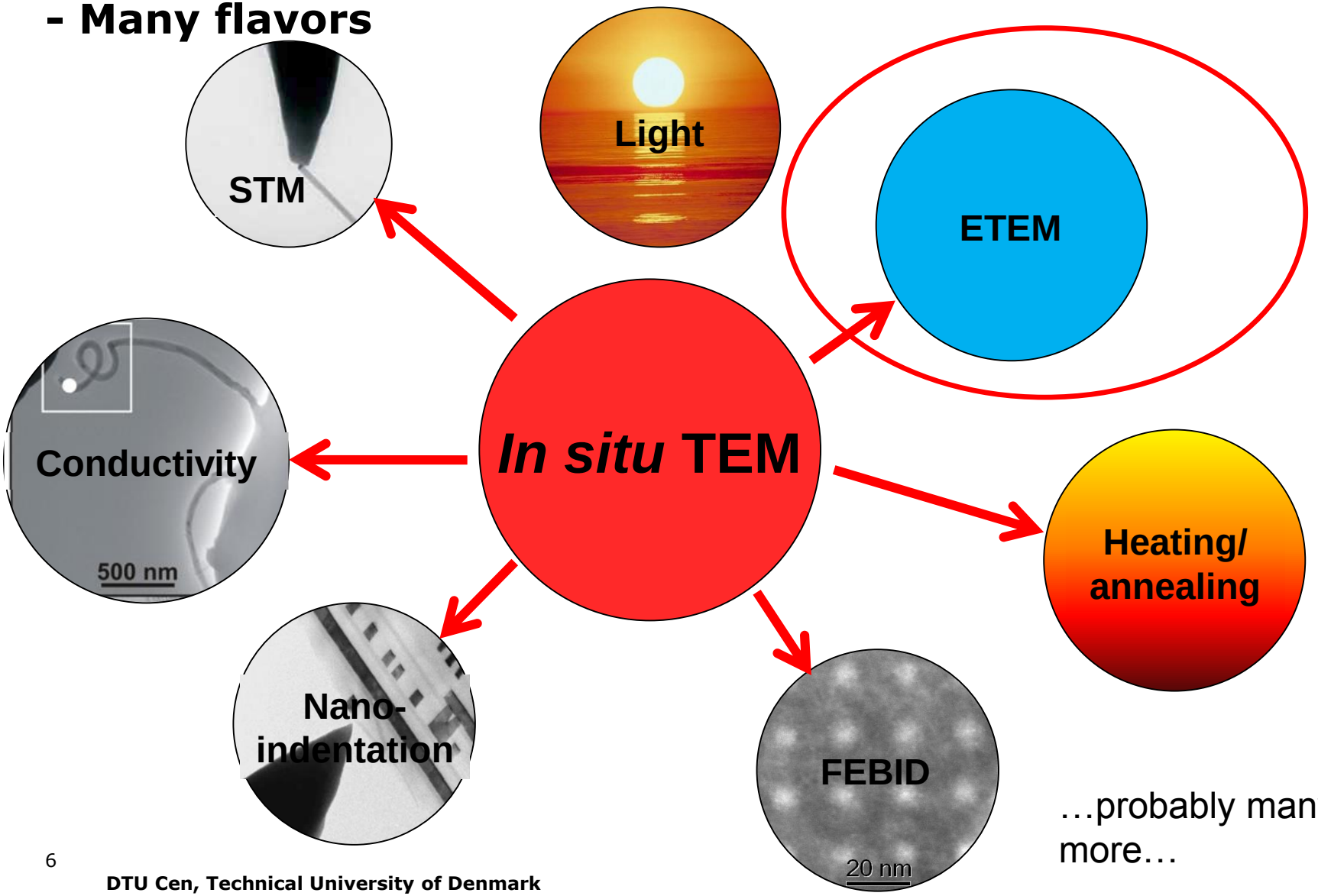
In Situ Techniques



Evolution of activity of industrial HDS catalysts,
B.M. Moyse, World Refining Jan/Feb (2001) 28
H. Topsøe, J. Catal. 216, 155 (2003)

- *In situ* XRD
  - Phase determination
  - Good for large areas
- *In situ* EXAFS, FTIR
  - Coordination
  - Chemical bonding
- Average values
  - No local information
- *In situ* TEM
  - Gives local information
- Etc…

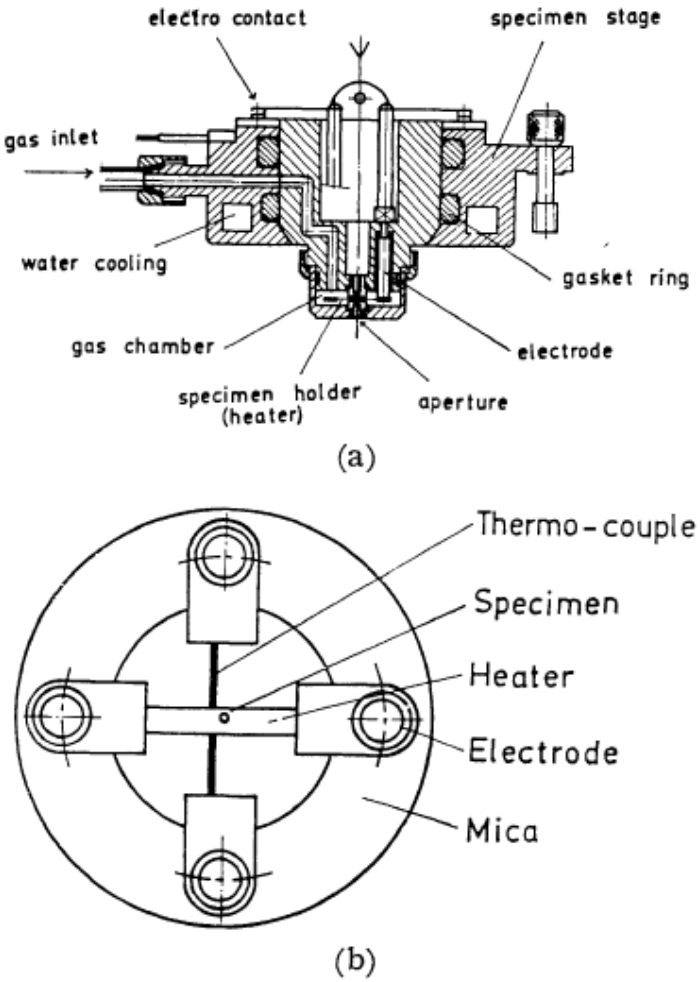
In Situ Microscopy
- Many flavors



…probably many more…

Historical Overview of ETEM

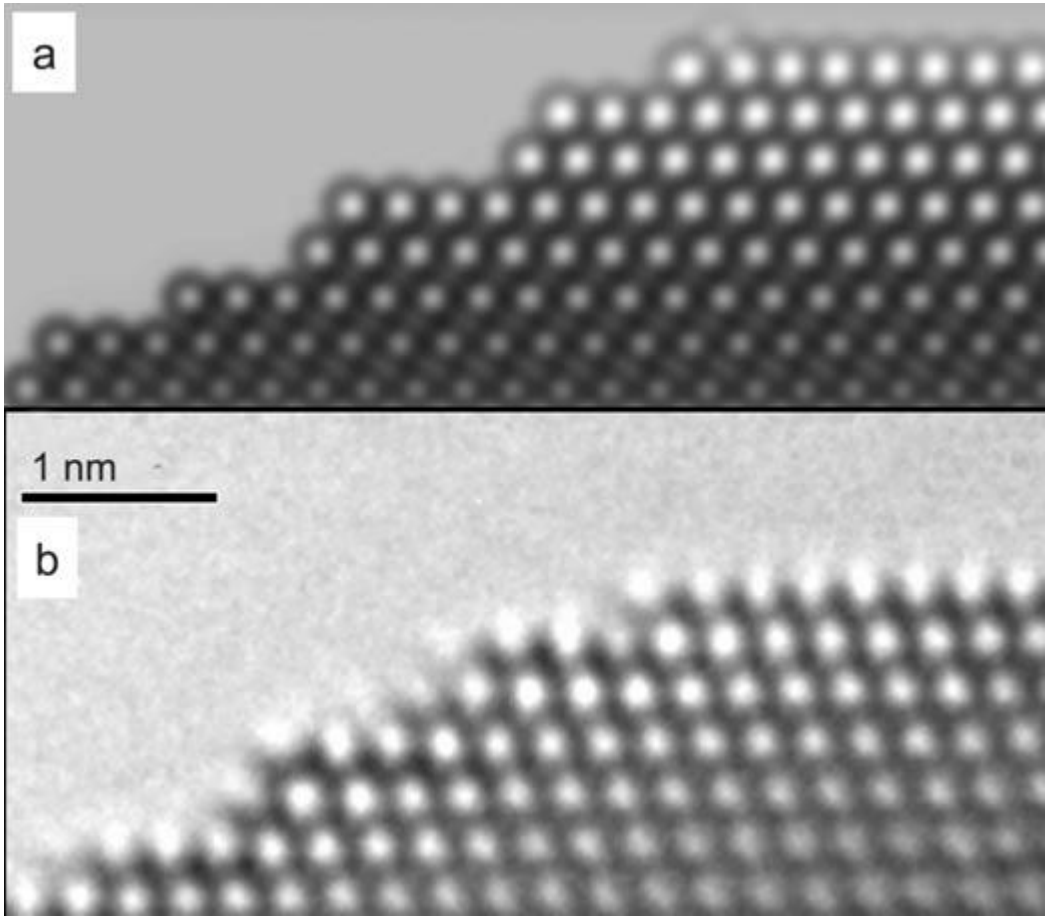
- Ambient temperature gas stages
  - E. Ruska: Kolloid. Zeit. 100, 212 (1942)
- Heating stages
  - P.B. Hirsch and A. Howie *et al.*: *Electron microscopy of thin crystals* (1965)
- The pioneers of environmental TEM
  - First E-cells: Hashimoto *et al.* Jpn. J. Appl. Phys. 7, 946 (1968) (older conference paper)
  - Catalysis work: Baker and Harris
    - Carbon deposits
    - Sintering
- The differentially pumped system we know today: E.D. Boyes and P.L. Gai, Ultramicroscopy 67, 219 (1997)
    - Differential pumping built into the TEM column



Source: Hashimoto *et al.* Jpn. J. Appl. Phys. 7, 946 (1968)

What are We Trying to Achieve?

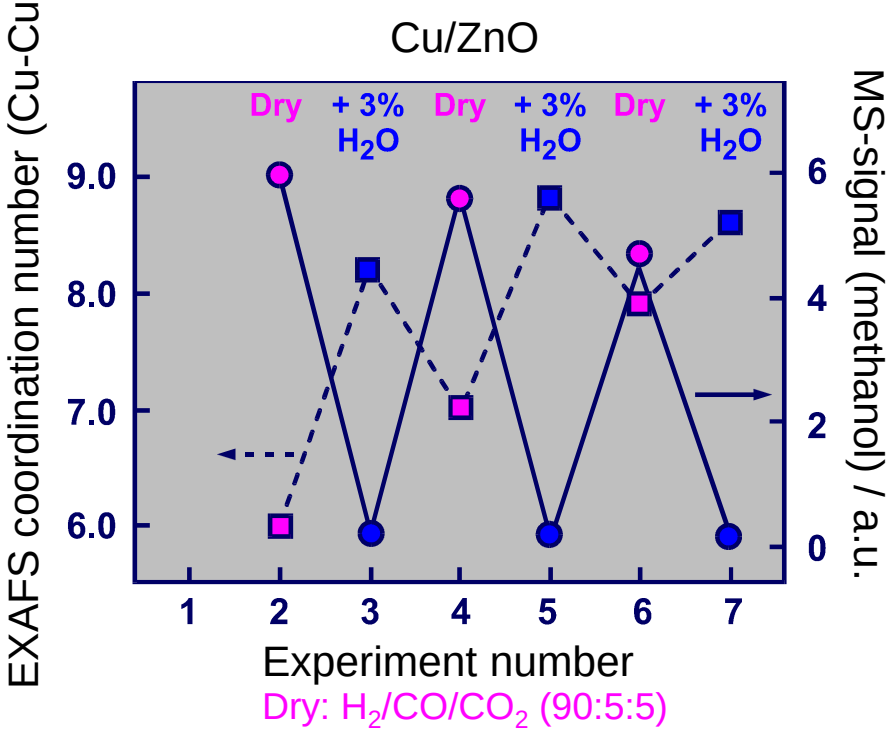
- Obtain high-resolution information
- Dynamic responses of materials as they are exposed to reactive gases at elevated temperatures
- Surface structure of materials in various environments
- Morphology of materials in different surroundings



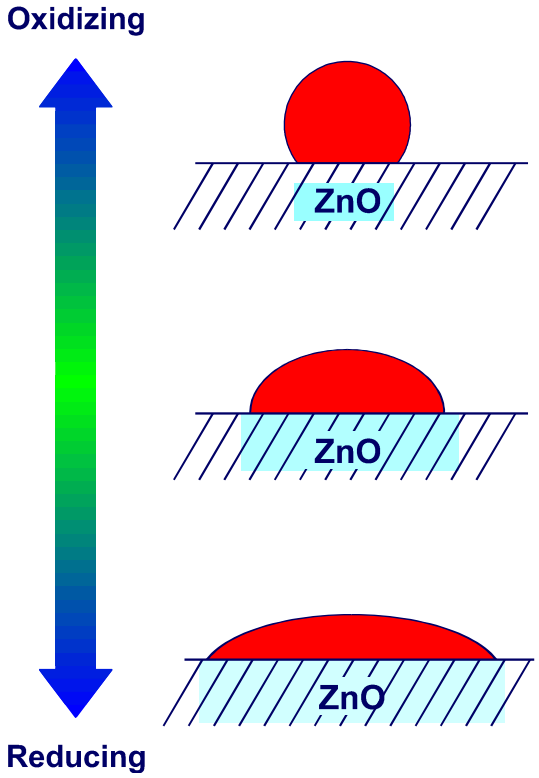
D. S. Su, T. Jacob, T. W. Hansen, D. Wang, R. Schlögl, B. Freitag, and S. Kujawa, *Angew. Chem.* **47**, 5005 (2008)

Methanol Synthesis
- a structure-sensitive reaction

$3\ H_2 + CO_2 \leftrightarrow CH_3OH + H_2O$
$CO + 2H_2 \leftrightarrow CH_3OH$
$CO_2 + H_2 \leftrightarrow CO + H_2O$



Grunwaldt *et al., J. Catal.* 194, 452 (2000)

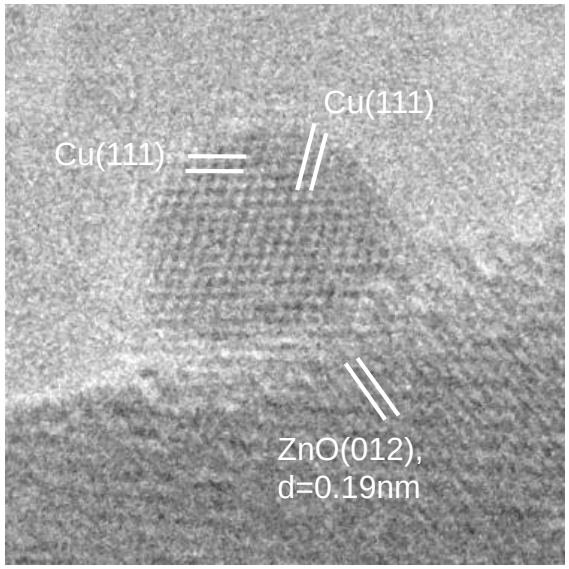


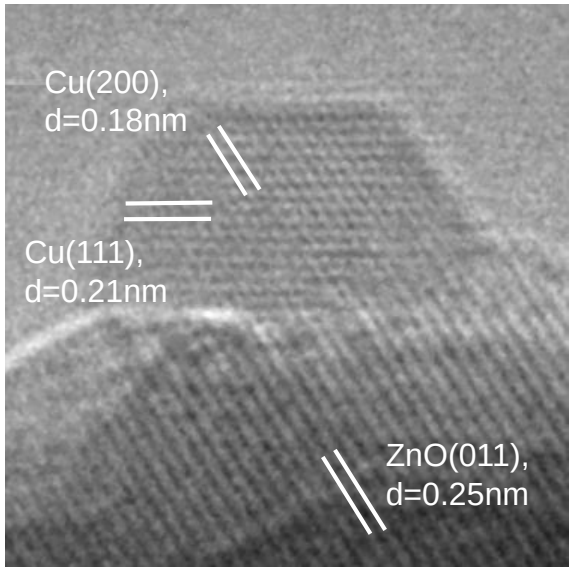
Clausen *et al., Topics Catal.* 1, 367 (1994)

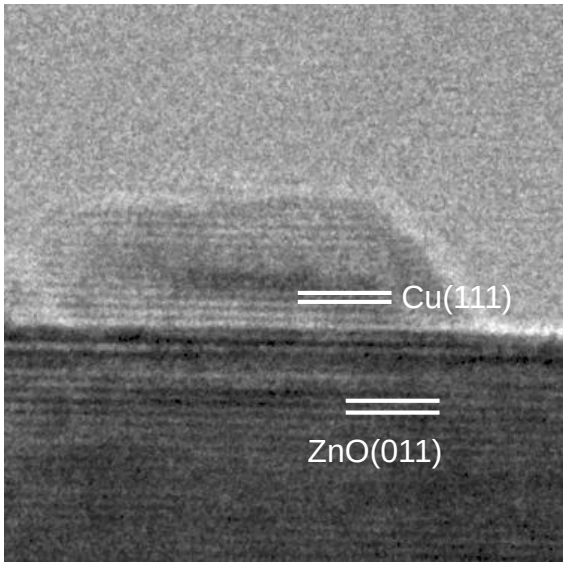
Can *in situ* HR-TEM unravel the details?

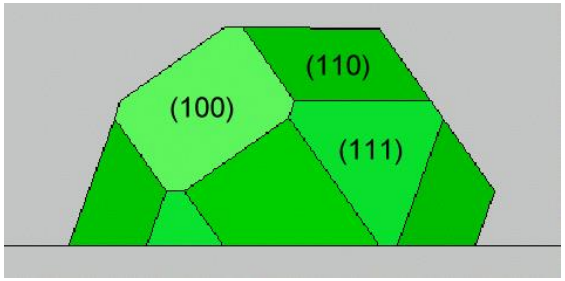
Equilibrium Shapes versus Gas Composition

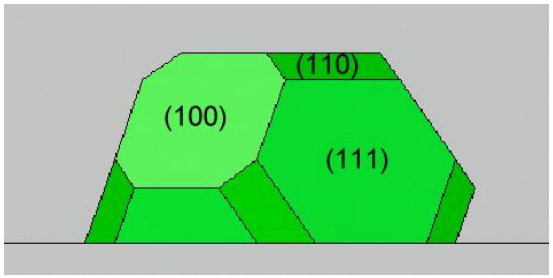
H_2/H_2O ⇄ H_2 ⇄ H_2/CO

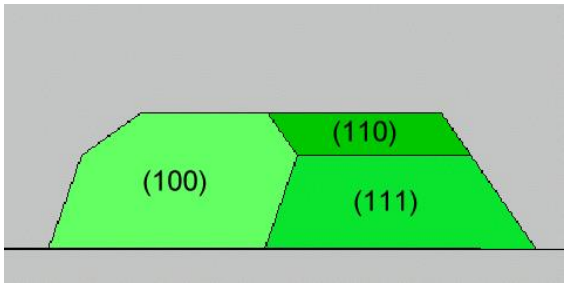












1.5mbar, H_2/H_2O=3/1, 220°C | 1.5mbar, 220°C | 1.5mbar, H_2/CO=95/5, 220°C

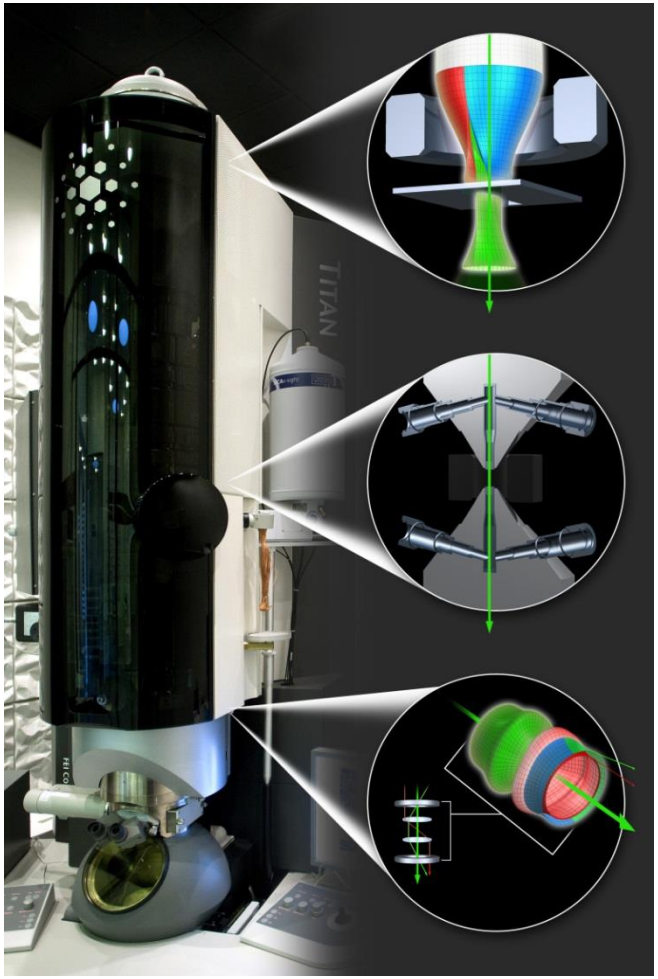
More oxidizing ⟷ More reducing

P. L. Hansen, J. B. Wagner et al. Science **295**, 2053-2055 (2002)

ENVIRONMENTAL TRANSMISSION ELECTRON MICROSCOPE DESIGN

The Environmental TEM

- Methods - instrumentation



Column Design

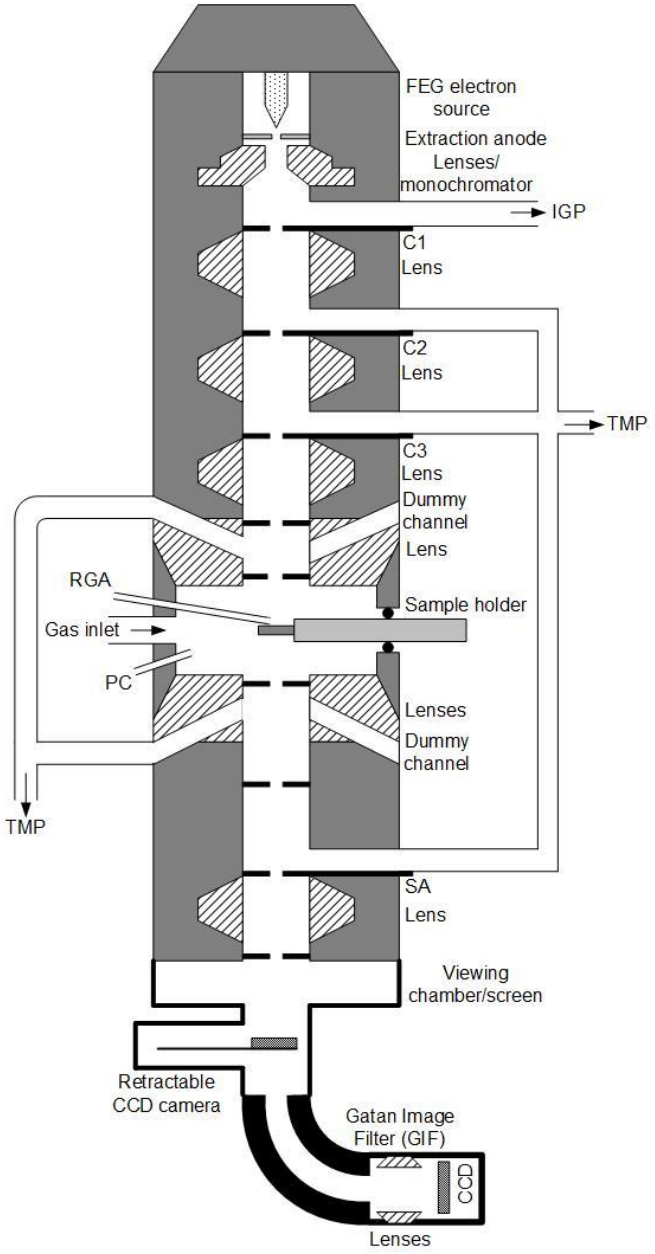
- Monochromated FEG electron source

- Differential pumping system
  1. Gas is leaked in (<10Nml/min)
  2. First set of diffusion limiting apertures
  3. Turbo molecular pump
  4. Second set of diffusion limiting apertures
  5. Turbo molecular pump
  6. Ion getter pump (IGP)

- Flow build up pressure (<2000Pa)

- Pressure at FEG source (<10^{-7}Pa)

- Direct line of sight!

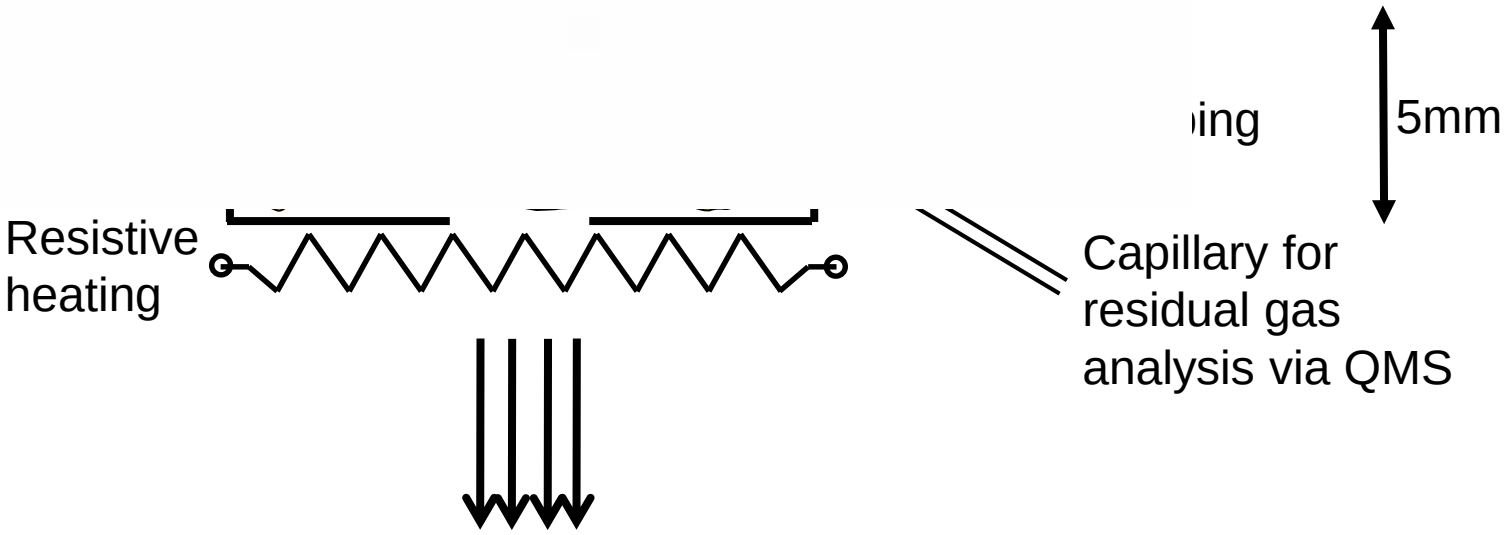


T.W. Hansen, JBW *et al.*, Mater. Sci. Technol. 26, 1338 (2010)

The Environmental Cell
- not really a cell…

- Main
  samp
  direct

React
gas



What is Environmental TEM Not?

- It is NOT UHV science
  - We have a high degree of control of the gas composition and temperature inside the sample region, BUT, it is not a UHV chamber
- It is NOT *operando* microscopy/spectroscopy
  - We are limited in especially pressure. We cannot expose samples to the conditions found in real reactors (but we are getting closer)
- It is NOT large scale science
  - It is still microscopy. We are investigating very small quantities of material
  - Kinetics and reaction products are complicated to measure

Conditions (pressure gap)

- Orders of magnitude
  - Conventional TEM ~10^{-8}mbar
  - Environmental TEM ~10^{1}mbar
  - Closed cell holder in TEM ~10^{3}mbar
  - Bench scale reactors ~10^{3}mbar
  - Industrial reactors ~10^{5}mbar
- We have gone most of the way…

Imaging in the Fog
- How does the atmosphere affect imaging

Can we get a clear view...?

Question?

- If you have 1000Pa of gas in the sample region, how thick a sample of say, C or Ni does that correspond to?
  - Assume T = 300° C
  - C: 12u, density = $2.3 \times 10^6 g/m^3$
  - Ni: 59u, density = $8.9 \times 10^6 g/m^3$
  - Assume 10mbar in the E-cell
  - Assume pole piece gap = 5mm
  - Gas constant $R=8.3 \times 10^{-5}$ m^3 bar K^{-1} mol^{-1}

Solution

- Gas density:

$$pV = nRT \Rightarrow \frac{n}{V} = \frac{p}{RT}$$

$$\frac{n}{V} = \frac{0.01 bar}{8.3\times10^{-5}\,\frac{m^3 bar}{K\cdot mol}\times 300K} = 0.4\,\frac{mol}{m^3}$$

- In the sample region:

$$0.4\,\frac{mol}{m^3}\times 0.005m = 2.0\times10^{-3}\,\frac{mol}{m^2}$$

- Ni:

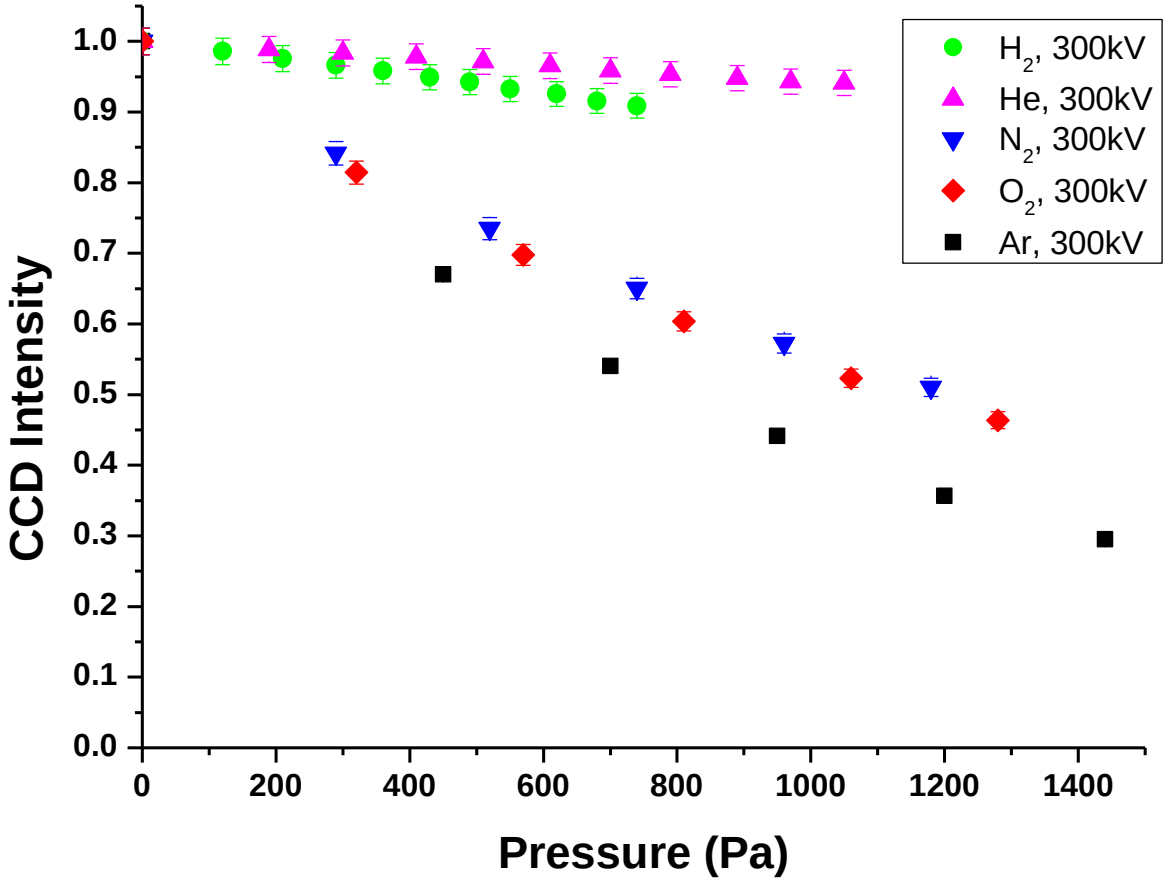
$$\frac{8.9\times10^{6}\,\frac{g}{m^3}}{59\,\frac{g}{mol}} = 1.5\times10^{5}\,\frac{mol}{m^3}$$

- Corresponding thickness:

$$\frac{2.0\times10^{-3}\,\frac{mol}{m^2}}{1.5\times10^{5}\,\frac{mol}{m^3}} \approx 10nm$$

Loss of Intensity

- Main effect of imaging in gas is loss of intensity
- Intensity measured on a bottom mounted camera
- Increasing pressure leads to loss of temporal resolution



T. W. Hansen and J. B. Wagner, *Microscopy and Microanalysis* 18, 684 (2012)

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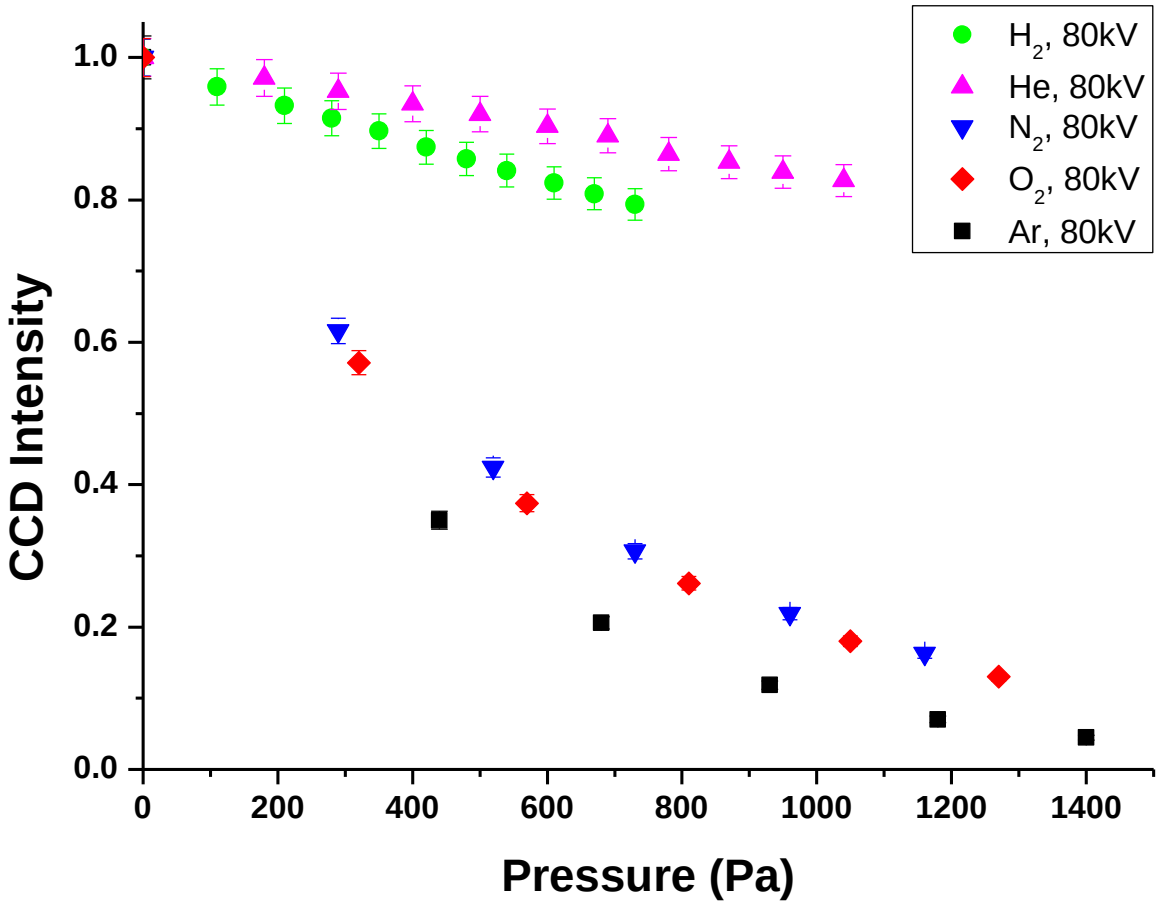
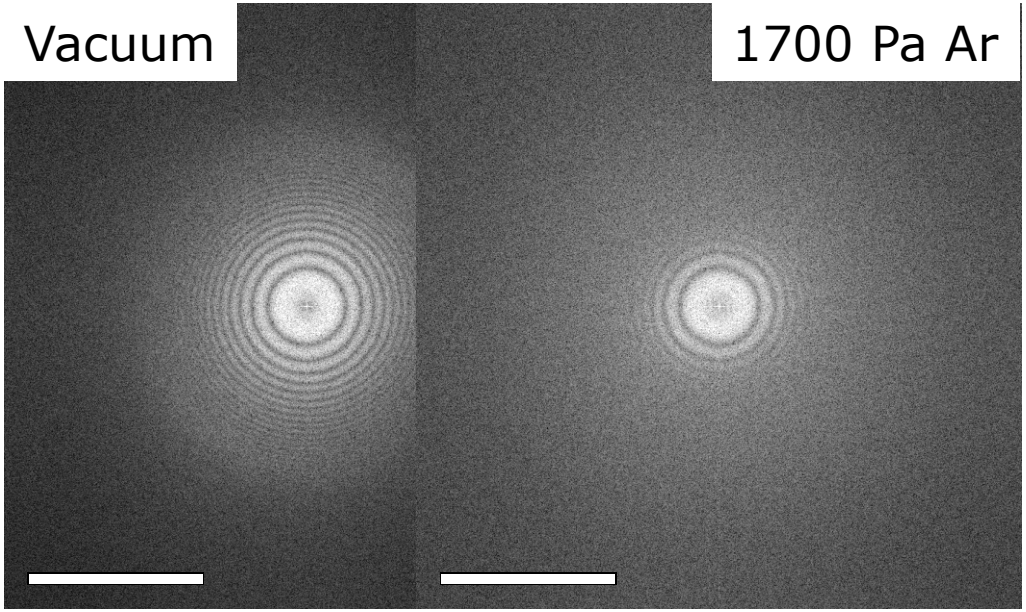
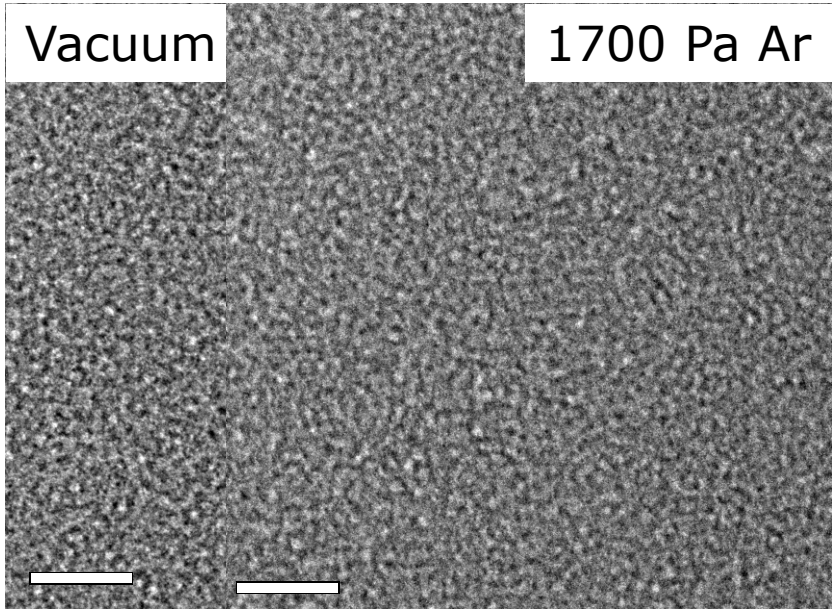


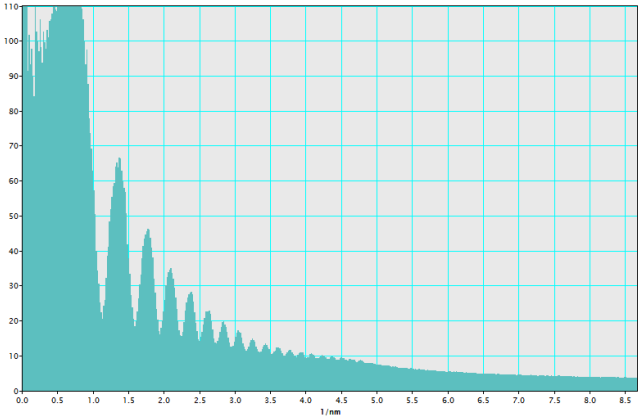
T. W. Hansen and J. B. Wagner, *Microscopy and Microanalysis* 18, 684 (2012)

CTF in the Presence of Gas

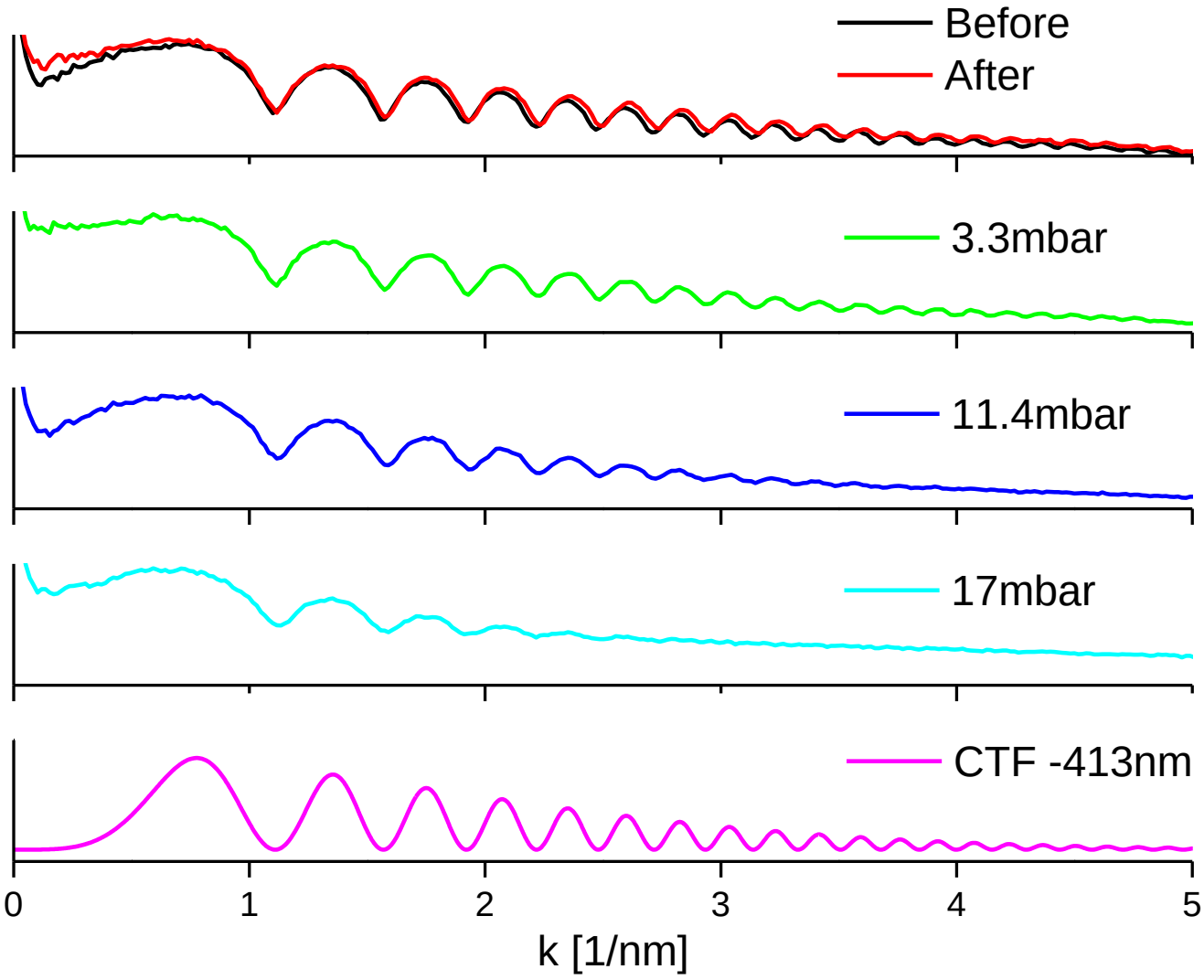
- Power spectrum of amorphous carbon film (imaged at -410nm defocus)







CTF in the Presence of Ar



Experimental Technicalities and Considerations

DTU Cen
Center for Electron Nanoscopy

Feeding gas to the E-Cell

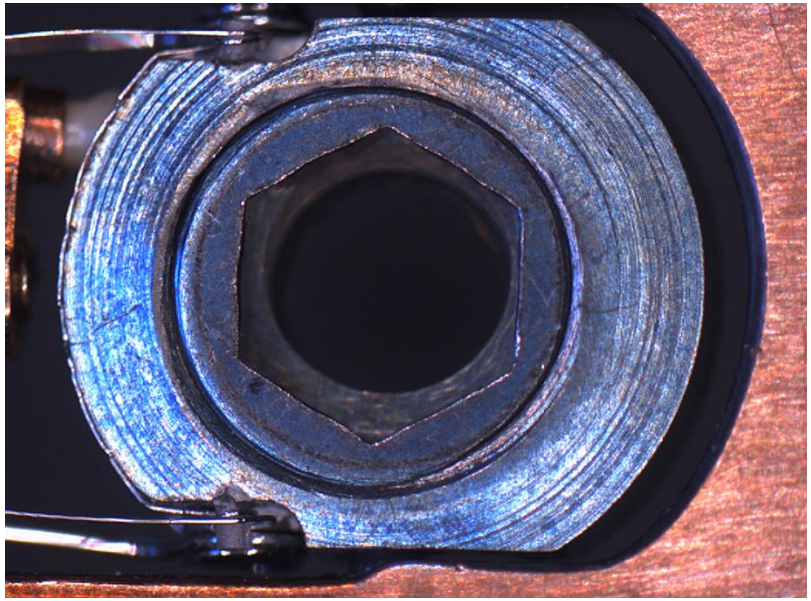
- Due to the minute power available from conventional heating holder, even small changes in the flow rate induces major temperature changes resulting in holder and sample drift
- The total flow in the E-cell is low compared to even bench scale reactors, thus small variations in flow can result in large deviations in partial pressures of the gas components
- A high degree of control is needed to ensure accuracy and resolution in your experiment
- Digital Mass flow controllers provide accurate control of the gas flow
- Do your gases react with each other?

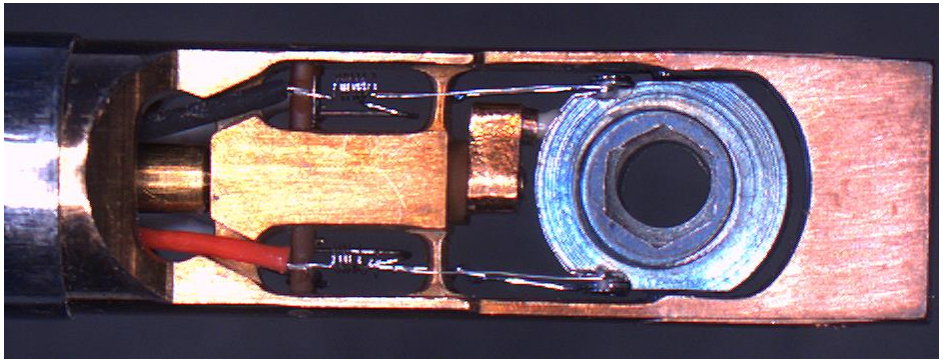
Cleanliness and Gases

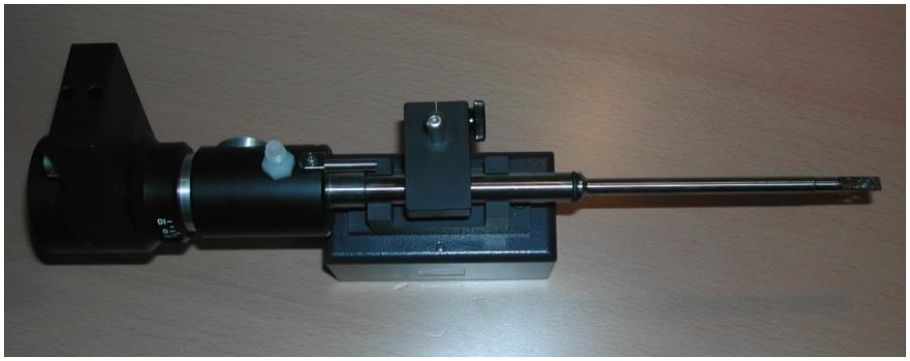
- Due to the low total pressure (~500 Pa) and flow (~5Nml/min), online monitoring of the gas composition is crucial
  - Leaks are crucial!
  - Desorption from pipe walls from earlier experiments
- Online mass spectroscopy can be used to monitor the gas composition during your experiment
- High purity gases should be used to minimize contamination in the system
  - Your sample will see whatever impurities you have in your gas supply or from leaks in the systems (e.g. O-rings)
- For general housekeeping in the sample region, *in situ* plasma cleaning can be used. This can also be used to remove hydrocarbon contamination on the sample surface
  - Take care! Does plasma cleaning effect your sample?
- Carrier gases are in general not used as this would significantly lower the partial pressures in the sample region and contribute to the overall contamination during the experiment

Holders

- Can provide heat to the sample
- In an ETEM:
  - Resistance to the atmosphere (e.g. oxidizing)
  - Limited power
  - Can be a problem to maintain temperature in a flowing gas
- Conventional holders are bulky and tend to drift during a heating ramp
- Alternatives
  - Laser heating
  - MEMS

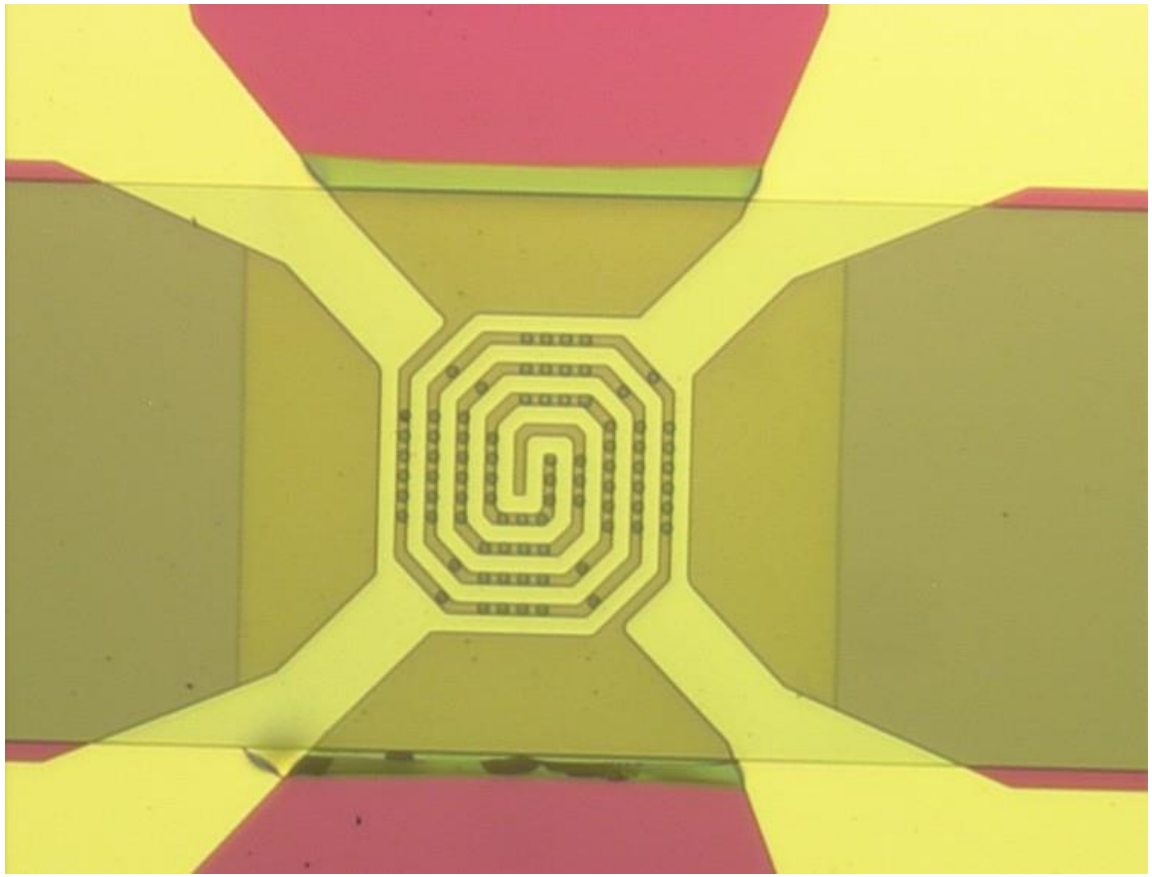






MEMS

- Micro Electro-Mechanical Systems
- Small area is heated
- Limited drift
- Fast heating and cooling ramps
- E.g. Protochips and DensSolution holder

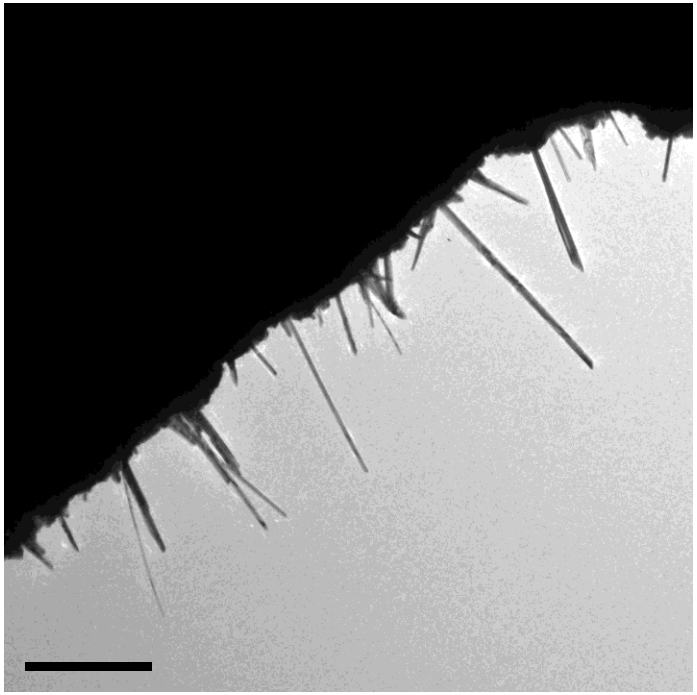


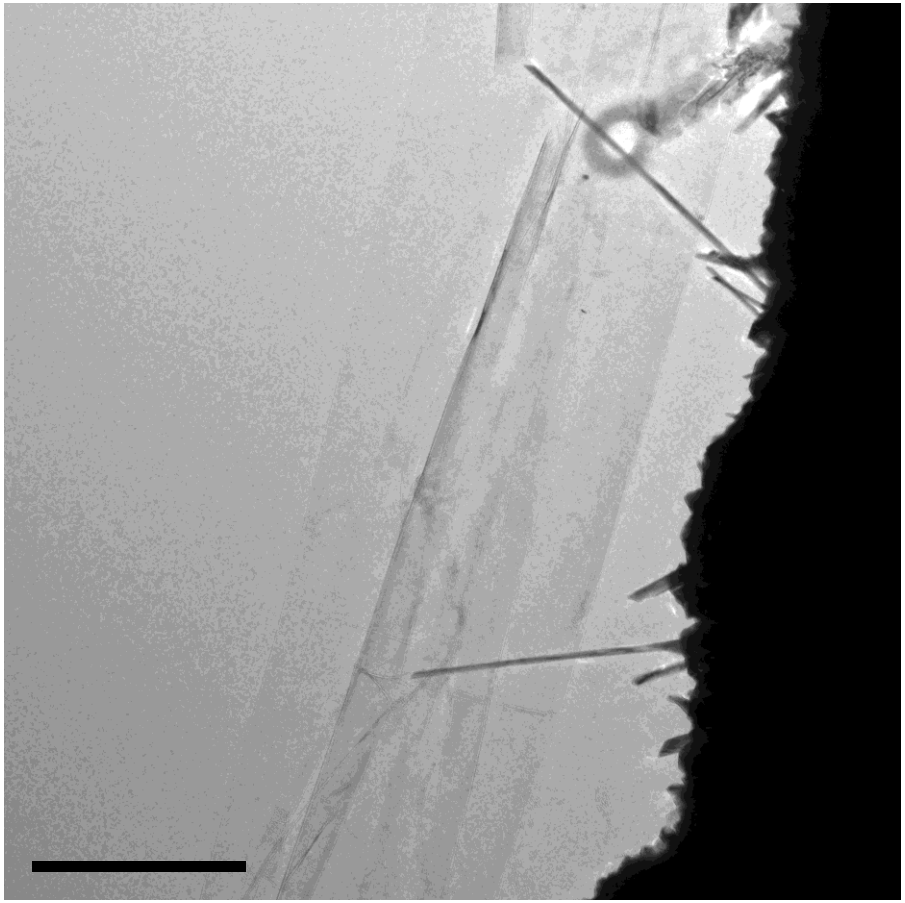
Grids

- Grids are usually chosen complementary to sample composition to ensure accuracy of spectroscopic data (EDX/EELS). Normally Cu grids are used (95% of sales)
- When doing *in situ* experimentation, grids must be chosen based on the conditions which the samples will be exposed to
- Things to consider:
  - Temperature. What is the melting temperature of the grid material?
  - Is the material prone to oxidation?
  - Will the grid in any way react with the gas phase in the E-cell?
- Some materials may have a significant uptake of gases
- "Use molybdenum grids for TEM studies when high temperature and inertness are needed" Quote from grid manufacturer.
  - Probably true, but not under an oxidizing atmosphere where volatile MoO_x species are formed

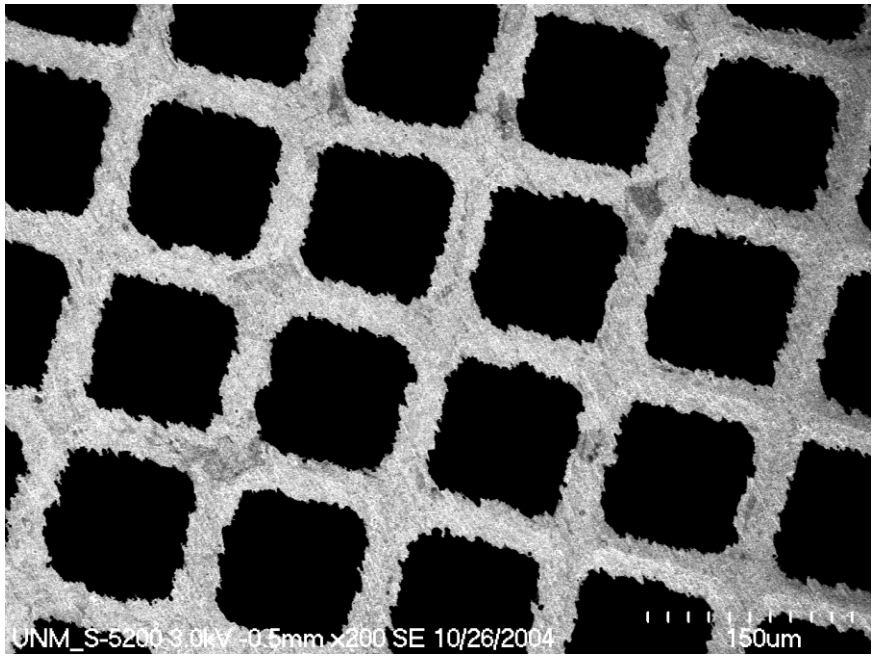
Cu Grids

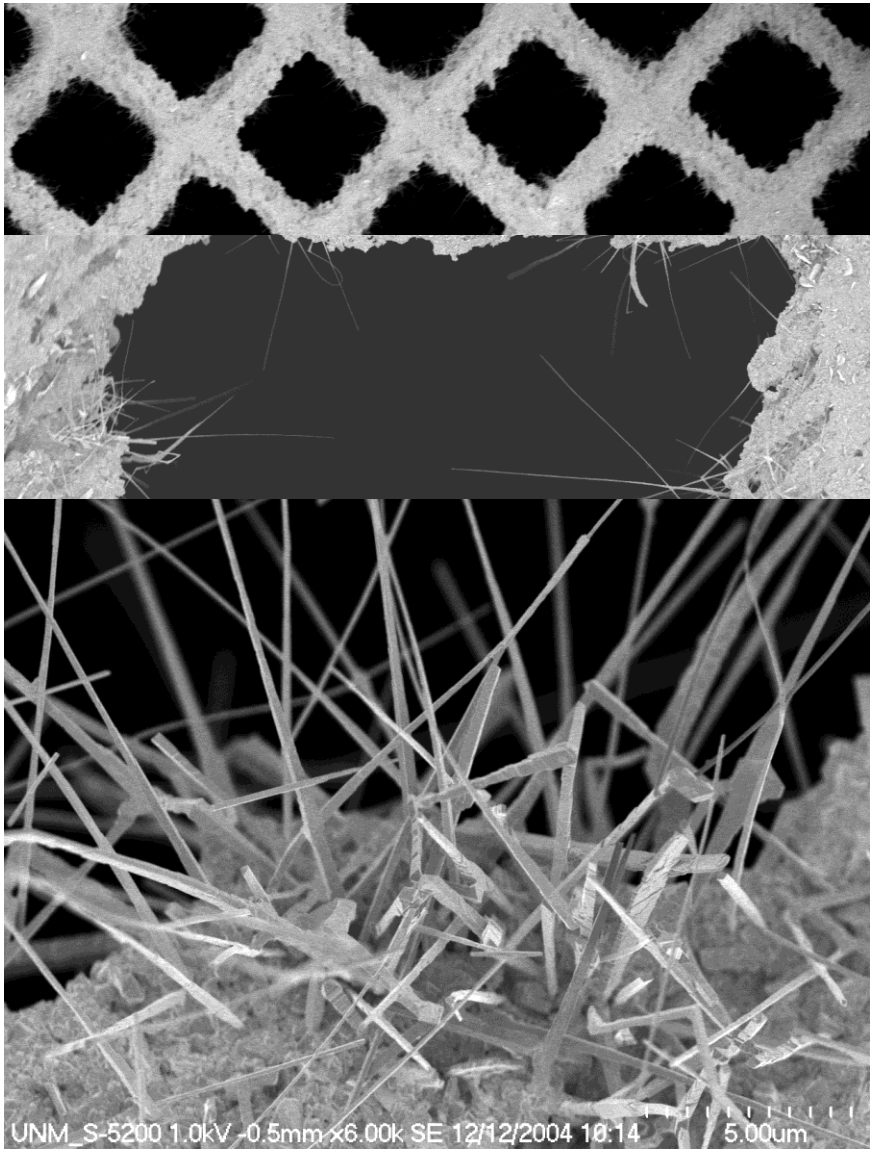
- Cu grid treated in O_2 at 500˚ C





Stainless Steel Grids...





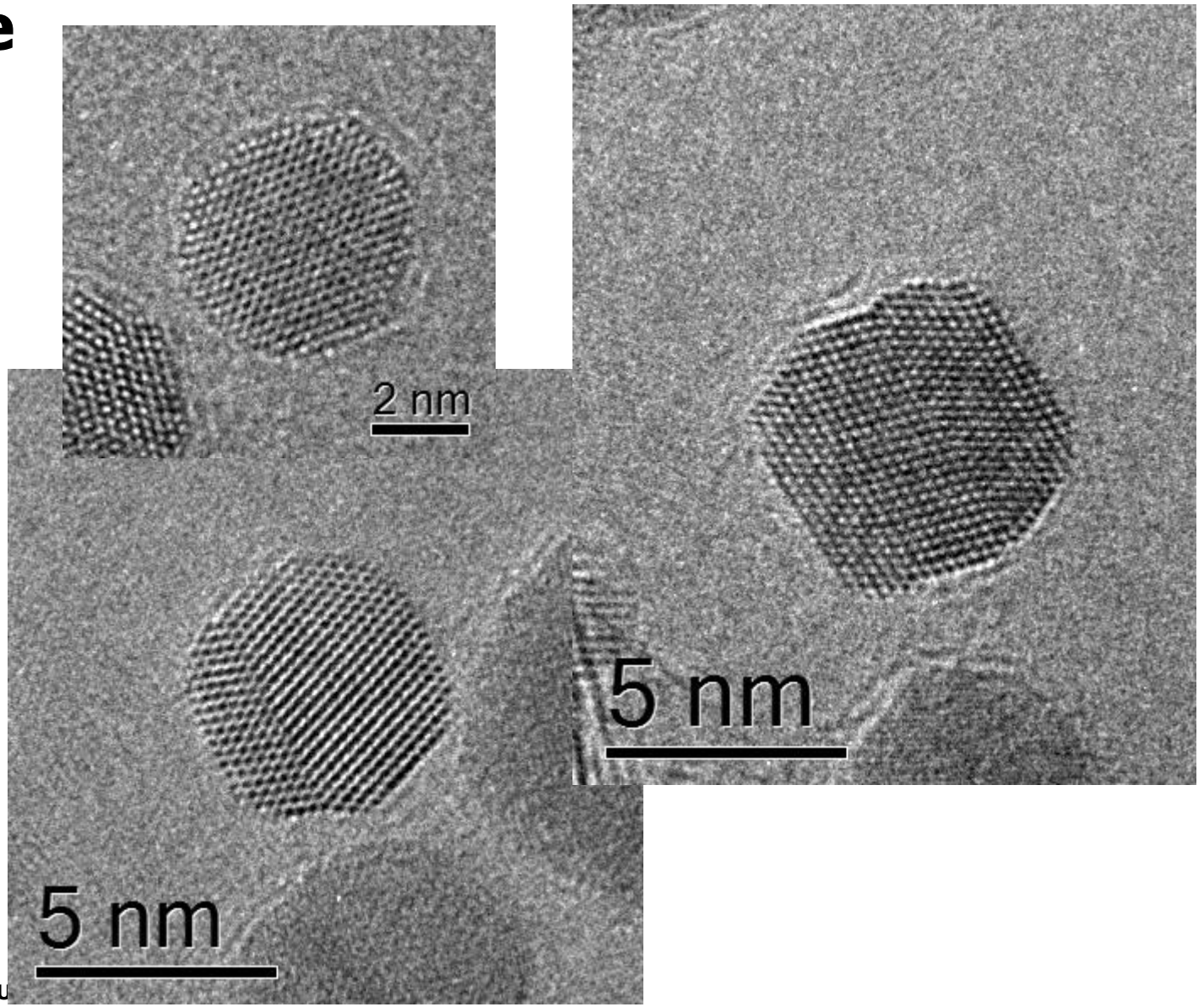
- Ca. 5mbar 50/50 H_2/H_2O at 750° C
- EELS shows Fe_xO_y
- ...not so stainless anymore...

Experimental Considerations:
Reference Experiments

- What do we expect to observe?
  - Assess or verify an observable effect in an external setup under the conditions in the ETEM prior to experimentation
  - Do things happen on a time scale feasible for ETEM experimentation?
- How can the effect of the beam be deconvoluted from the obtained data?
  - Verify validity of derived kinetic parameters, compare with numbers obtained from other techniques (never rely on a single technique)
  - Do ex situ investigations prior to time consuming environmental TEM studies
  - "Blind" experiments in the ETEM might elucidate a potential effect of the electron beam

Imaging Au in Hydrogen at Increasing Pressure

- Au on graphene
- P=10^{-6}mbar
- P=2.9mbar
- P=4.3mbar



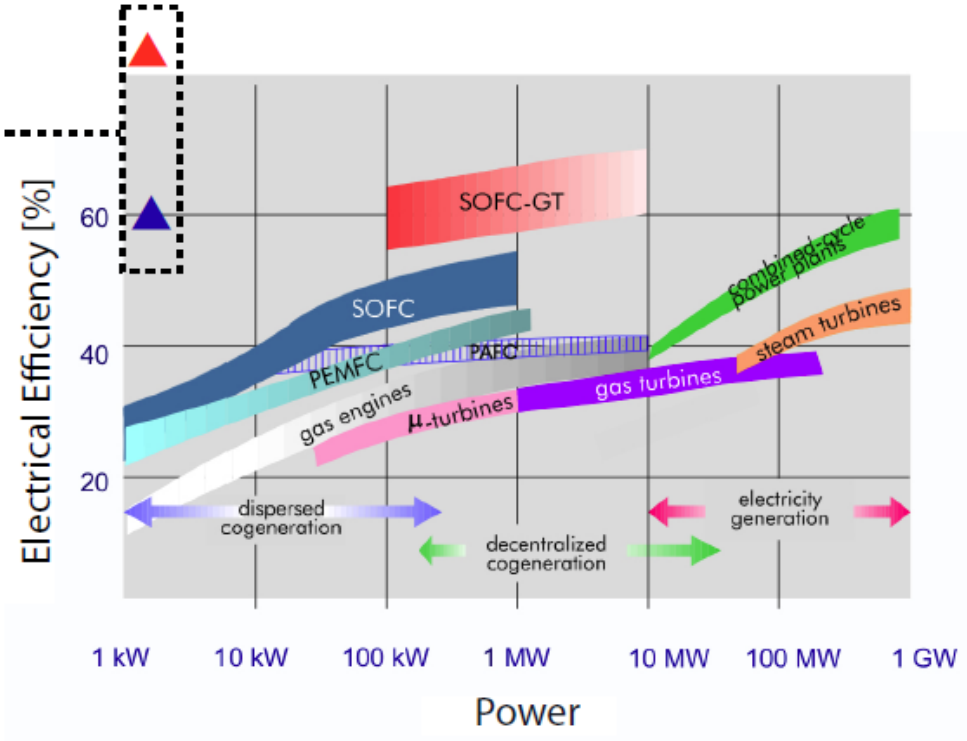
APPLICATIONS

Solid Oxide Fuel Cells

In 2009:

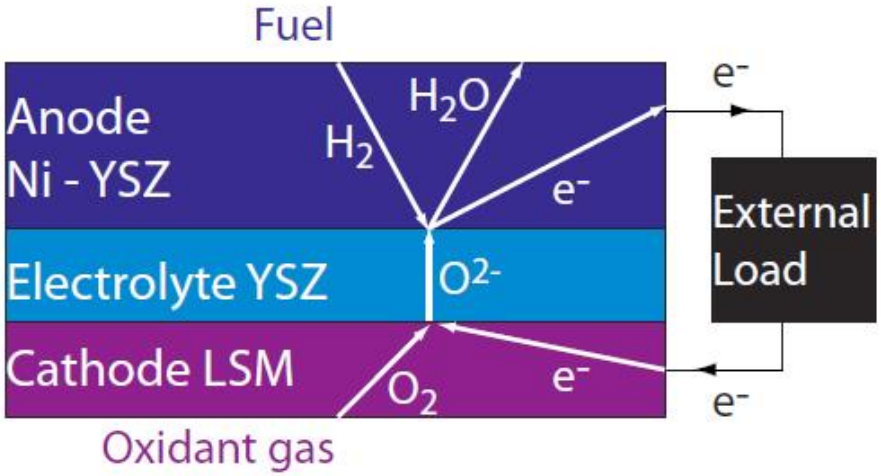
▲ 60% electrical efficiency achieved with SOFC alone in a 1.5 kW stack [1]

▲ 85% total efficiency (recover heat from the fuel cell for hot water)

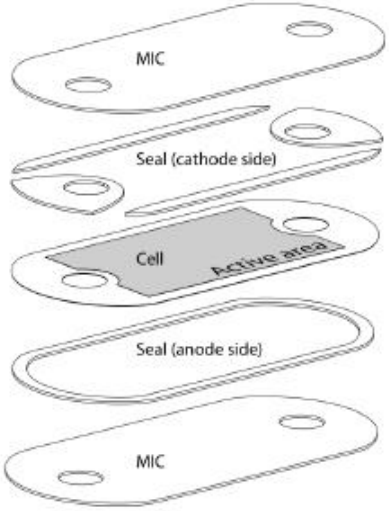


Data from 2001 from the company Alstom

Solid Oxide Fuel Cells

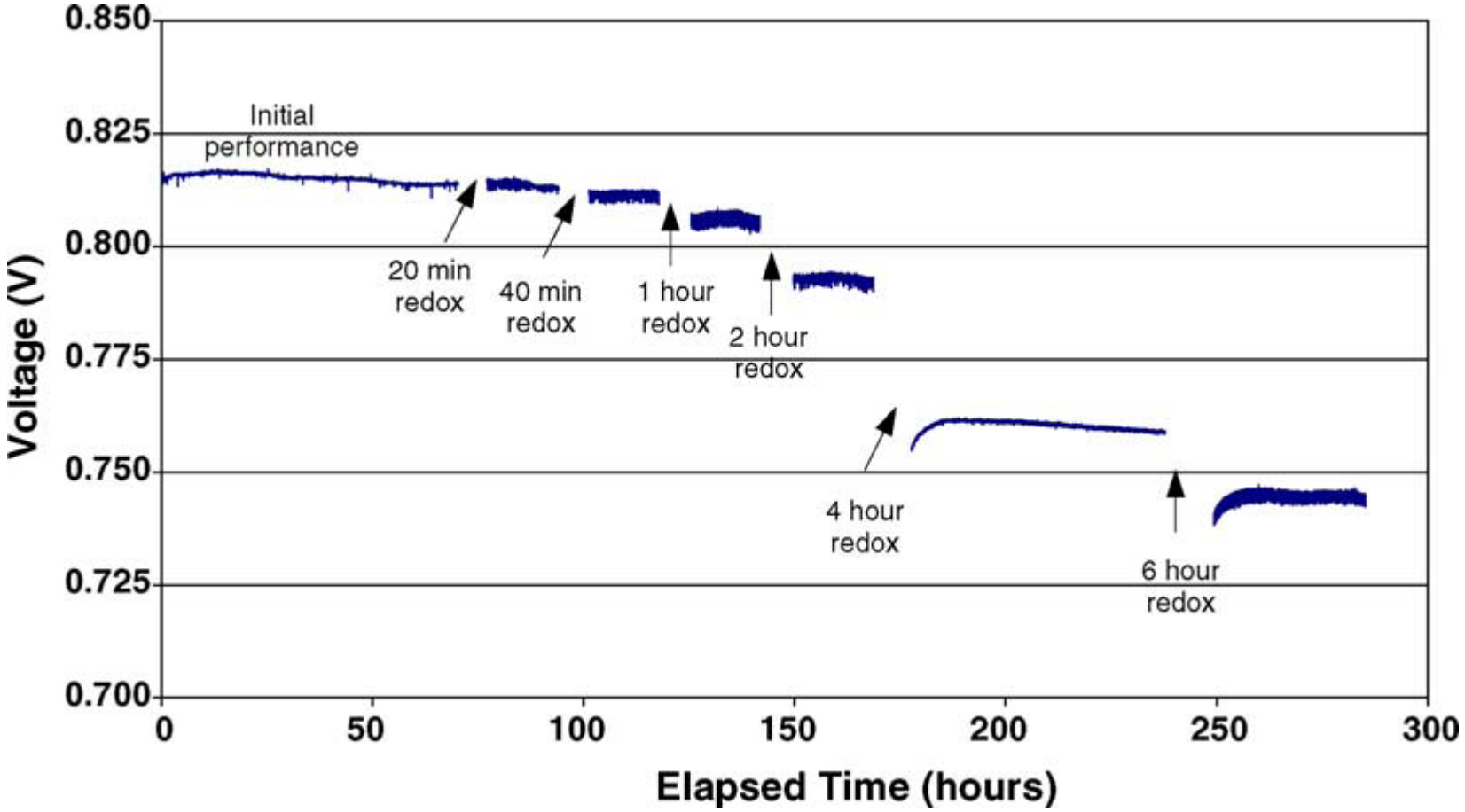


H_2O, excess fuel & oxidant gas
to burner, gas turbine and heat exchanger



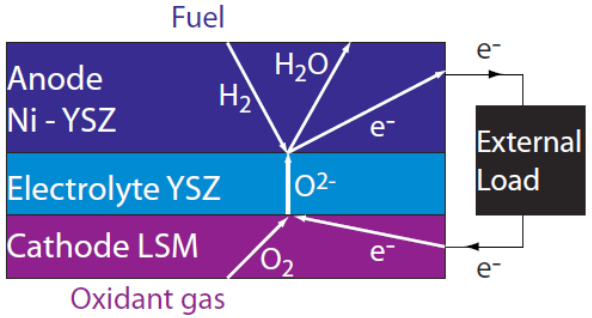
Fuel Cell Anode Failure

- Redox stability of NiO/YSZ based anode

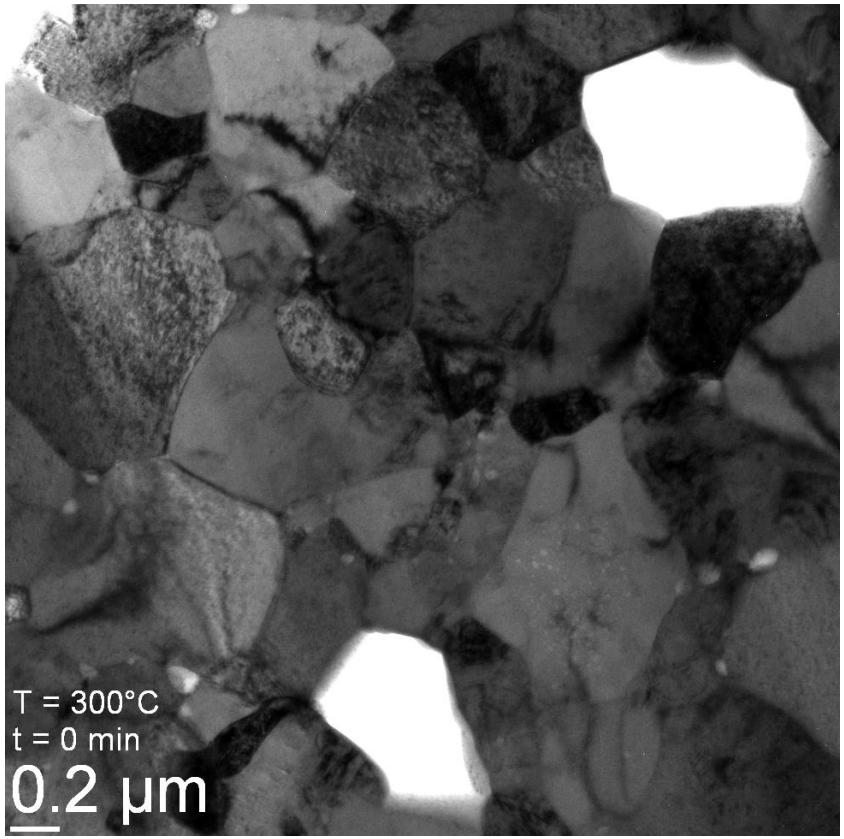


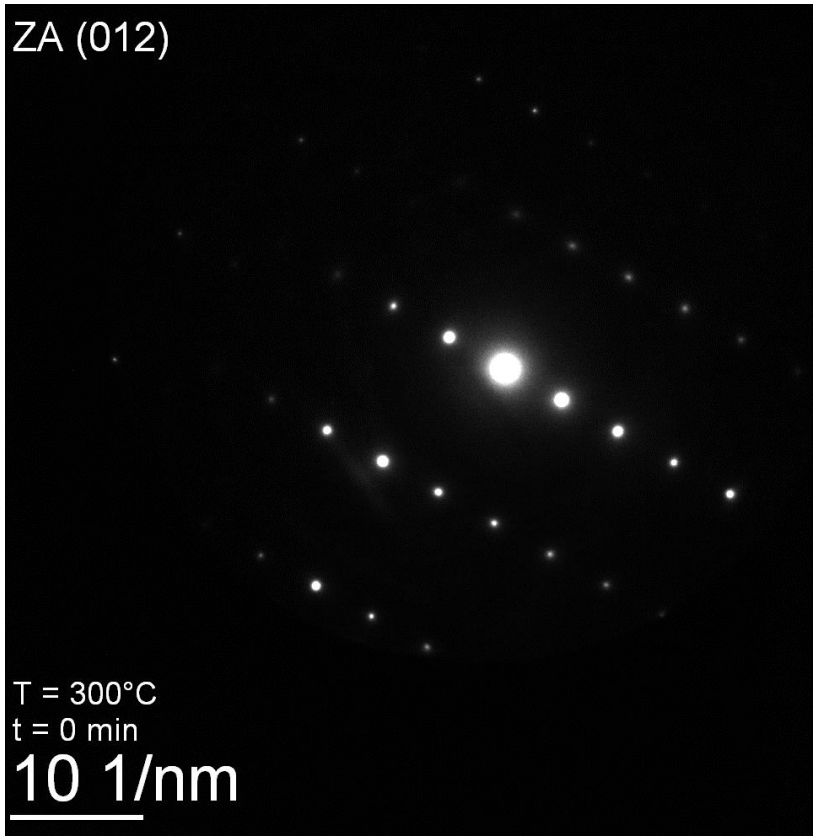
Q. Jeangros *et al., Acta Mater.* **58**, 4578 (2010)

In Situ Red(ox) Process of Solid Oxide Fuel Cell Anode



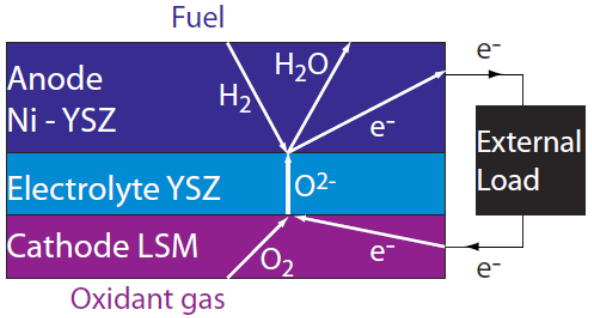
Reduction
150Pa H_2



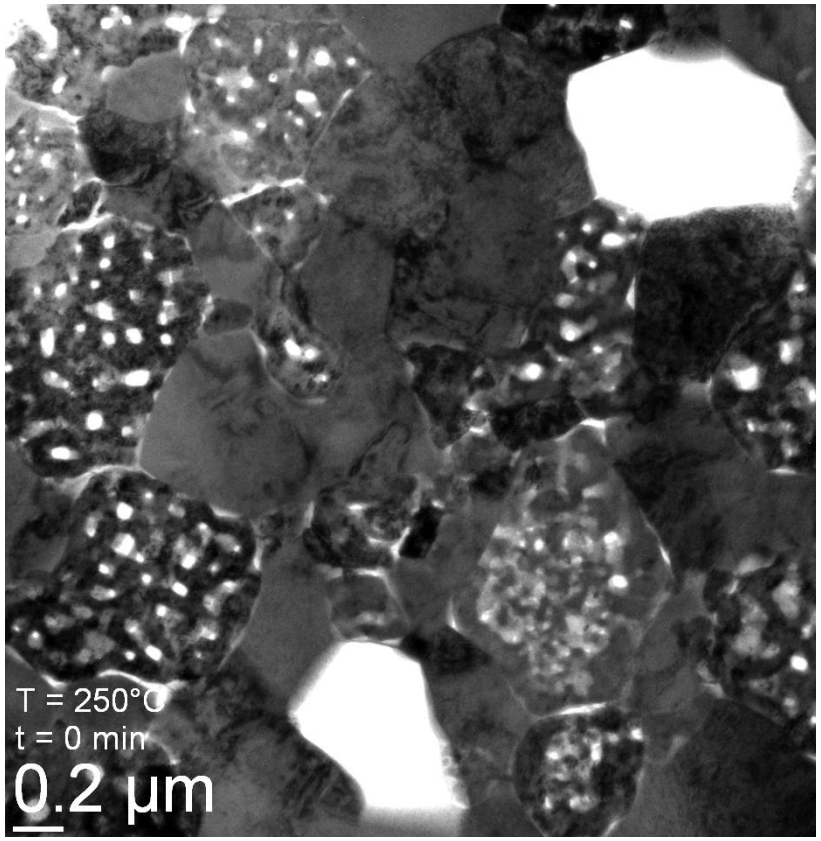


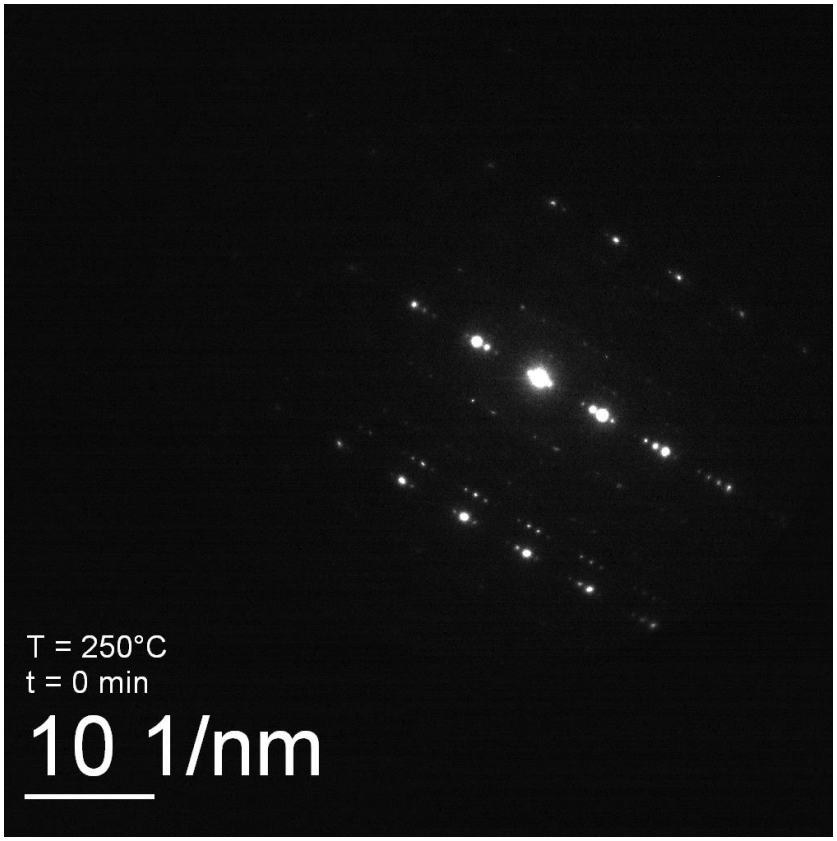
Q. Jeangros, JBW *et al., Acta Mater.* **58**, 4578 (2010)

In Situ (Red)ox Process of Solid Oxide Fuel Cell Anode



Oxidation
320Pa O_2



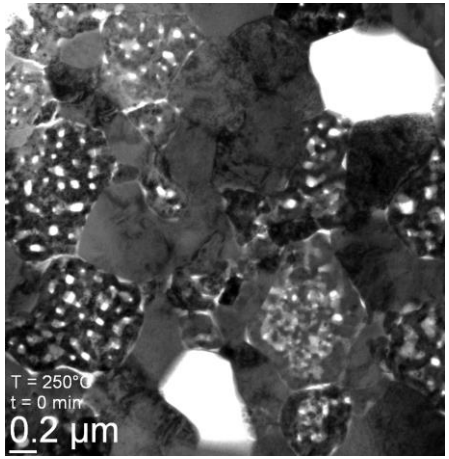


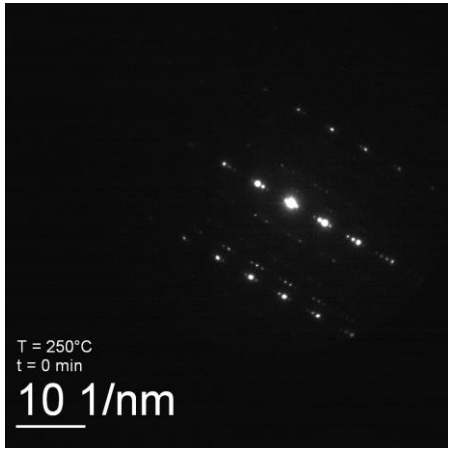
Q. Jeangros, JBW *et al., Acta Mater.* **58**, 4578 (2010)

Imaging at Different Length Scales
-2D to 3D and irreversible changes

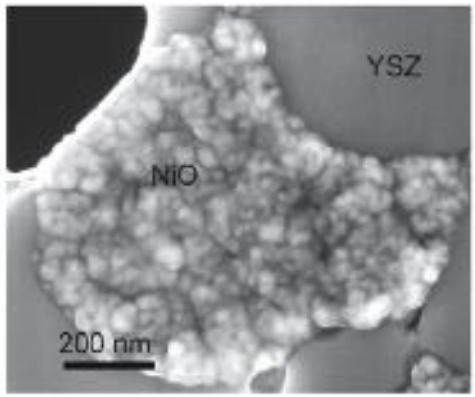
FIB slice of NiOx/YSZ based SOFC

ETEM

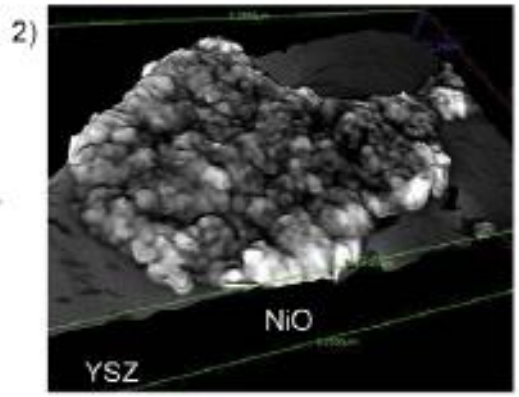




SEM



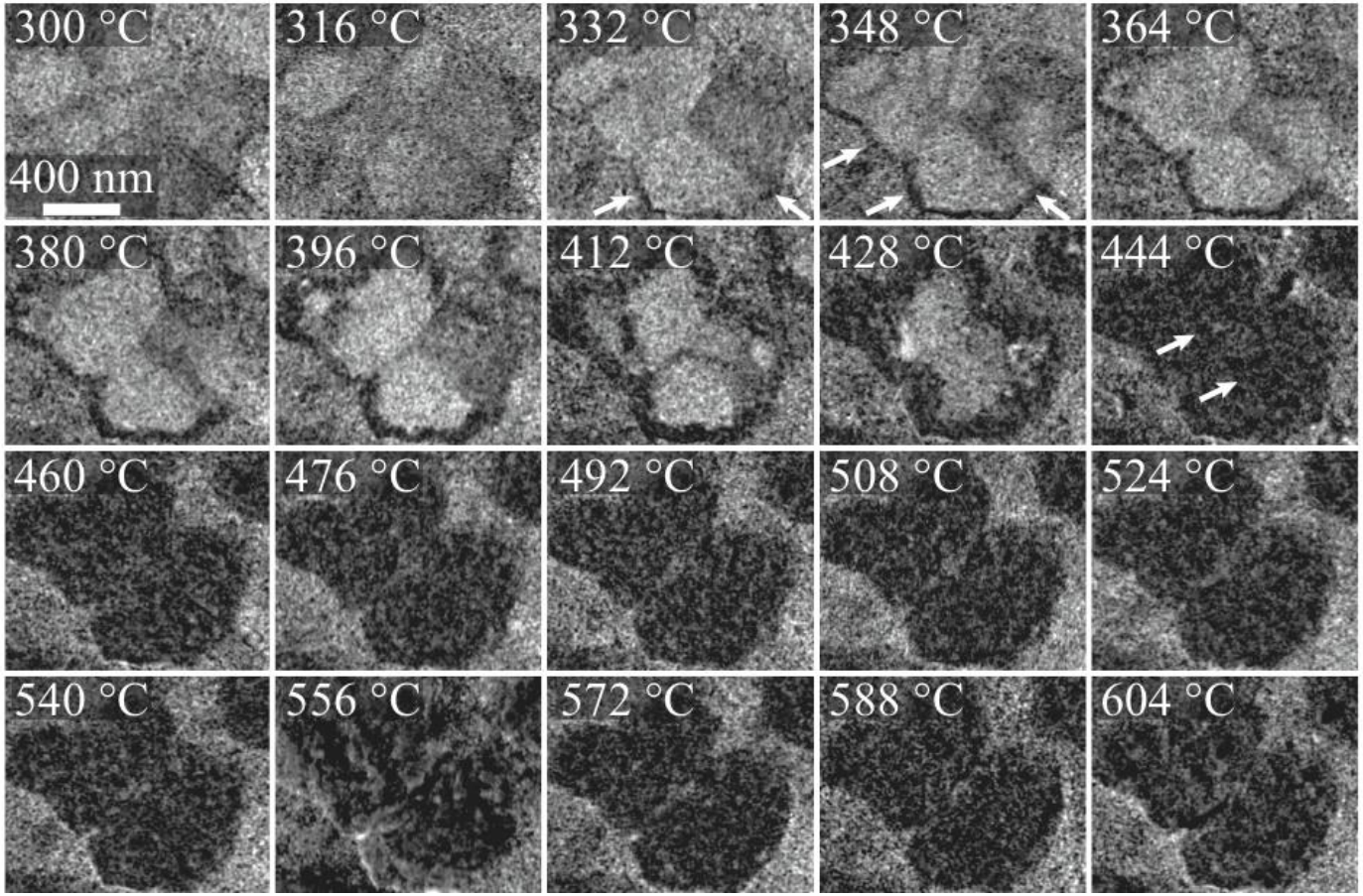
3D



Q. Jeangros, JBW *et al., Acta Mater.* **58**, 4578 (2010)

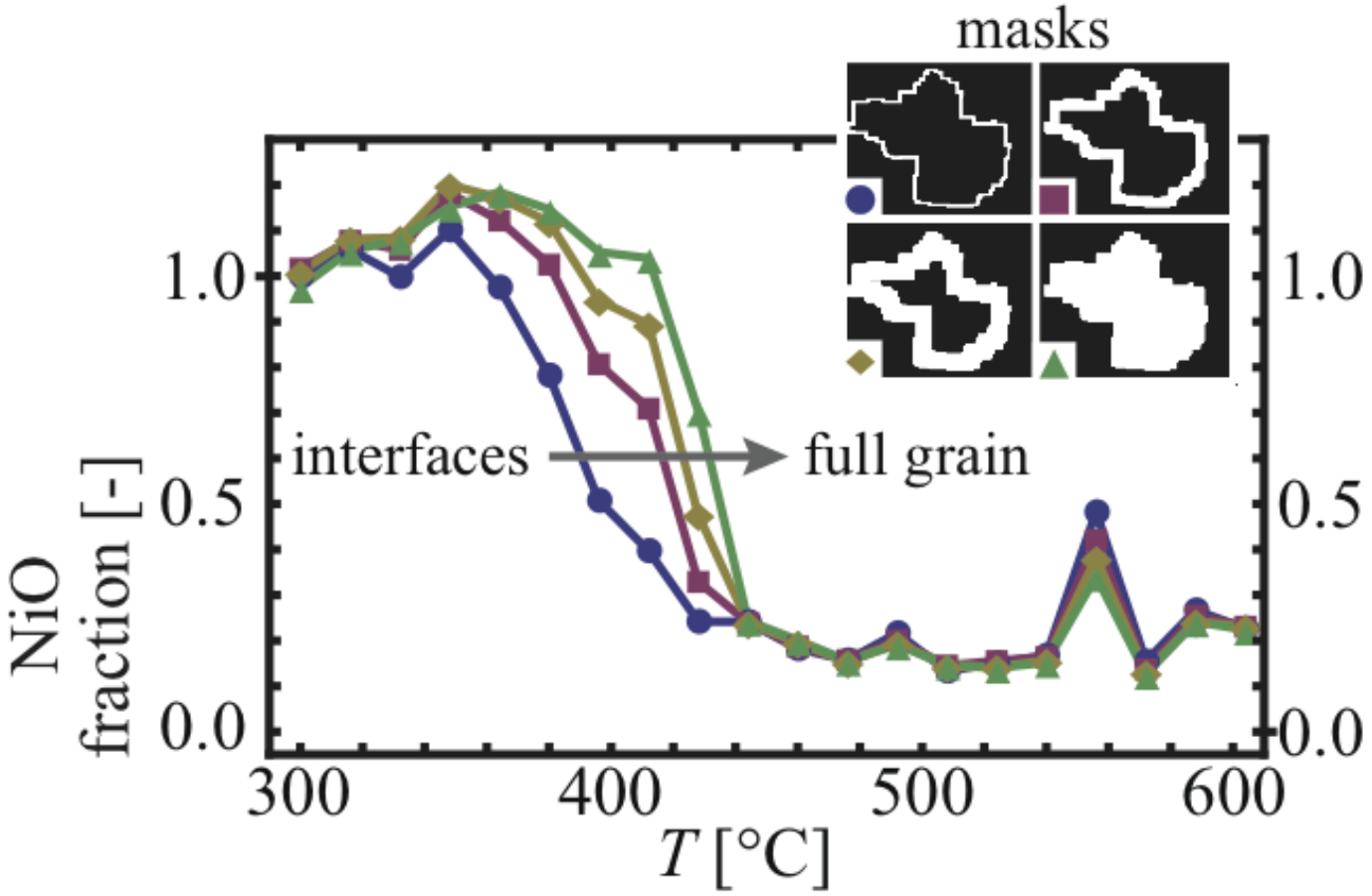
Reduction of NiO/YSZ

EFTEM imaging (O K edge), 2K/min heating ramp



Q. Jeangros, JBW *et al.*, Chem Commun. **50**, 1808 (2014)

Reduction of NiO/YSZ

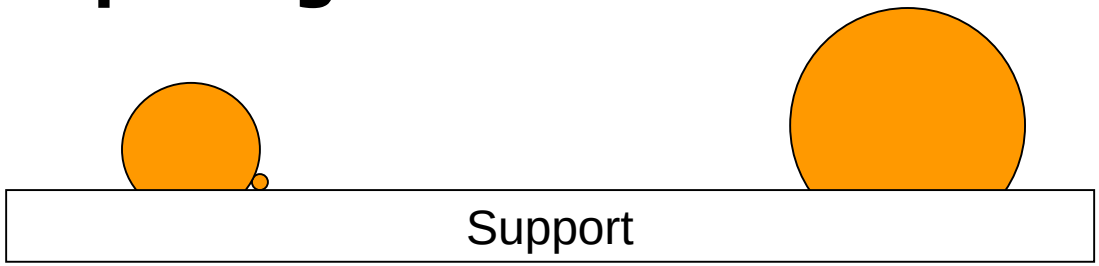


Q. Jeangros, JBW *et al.*, Chem Commun. **50**, 1808 (2014)

Catalyst Deactivation Mechanisms

- Catalysts are used in 90% of chemical reactions today
- ~15% of the GNP in the industrialized countries depends on catalysts
- Poisoning
  - Blockage of active sites by reactant molecules or contamination, e.g. S atoms
- Breakdown of the pellet structure
  - E.g. formation of carbonaceous filaments in steam reforming catalysts breaking the pellet structure from the inside
- Sintering
  - Growth of the active metal particles at the expense of surface area
  - One of the most important deactivation mechanisms in supported metal catalysis

Catalyst Deactivation:
Ostwald Ripening



$$\mu = \mu_0 + \frac{2\gamma_m \Omega}{r}$$

- Effectively, large particles grow on the expense of small particles
- Particle size distributions

Diffusion control

$$f_d(t,\tilde{d}) = \frac{c_d \phi_d(\tilde{d})}{(1 + t/t_d)}$$

$$\left(\frac{\bar{d}(t)}{\bar{d}(0)}\right)_d = (1 + c_d t)^{1/4}$$

Interface control

$$f_i(t,\tilde{d}) = \frac{c_i \phi_i(\tilde{d})}{(1 + t/t_i)}$$

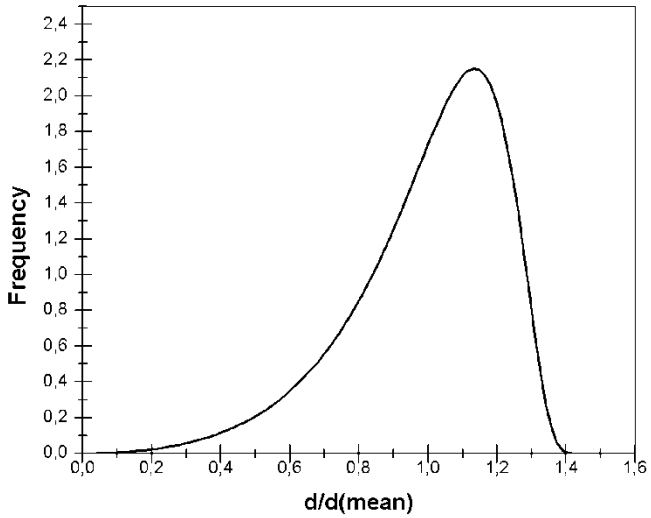
$$\left(\frac{\bar{d}(t)}{\bar{d}(0)}\right)_i = (1 + c_i t)^{1/2}$$

$$\tilde{d} = \frac{d}{\bar{d}}$$

J. A. Horsley *et al.*, *Stability of Supported Catalysts: Sintering and Redispersion* (Catalytica Studies Division, 1991)

Particle Size Distribution from Ostwald-Ripening

- Theoretically, particles sintered by O-R produce a PSD with a tail on the small-diameter side and a sharp cut-off to larger diameters
- *Time-independent* PSD:



$$\phi_{O-R}(\tilde{d}) = \frac{81 e \tilde{d}^2 \exp(1/(2\tilde{d}/3-1))}{\sqrt[3]{32}(\tilde{d}+3)^{7/3}(1.5-\tilde{d})^{11/3}}$$

R. Finsy, *Langmuir* **20**, 2975 (2004)

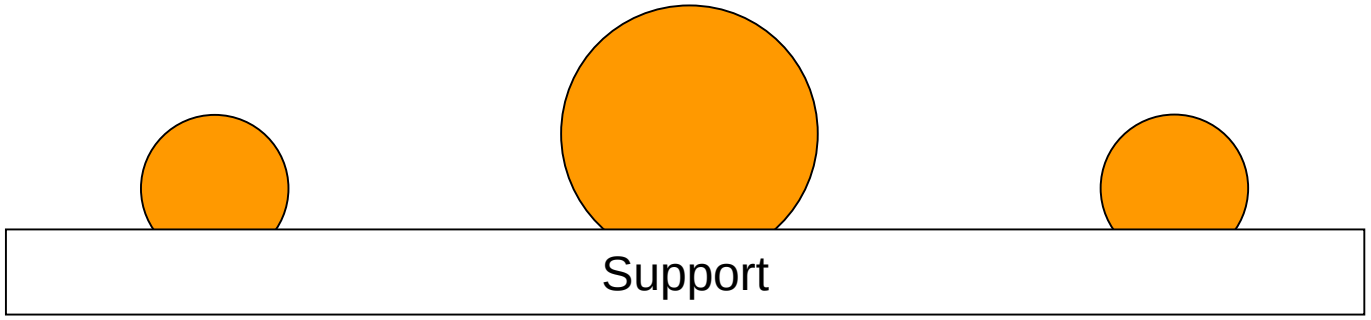
Catalyst Deactivation:
Particle Migration and Coalescence

Surface diffusion coefficient

$$D_s = D_0 \exp\left(\frac{-Q}{RT}\right)$$

Particle diffusion coefficient, Gruber formula

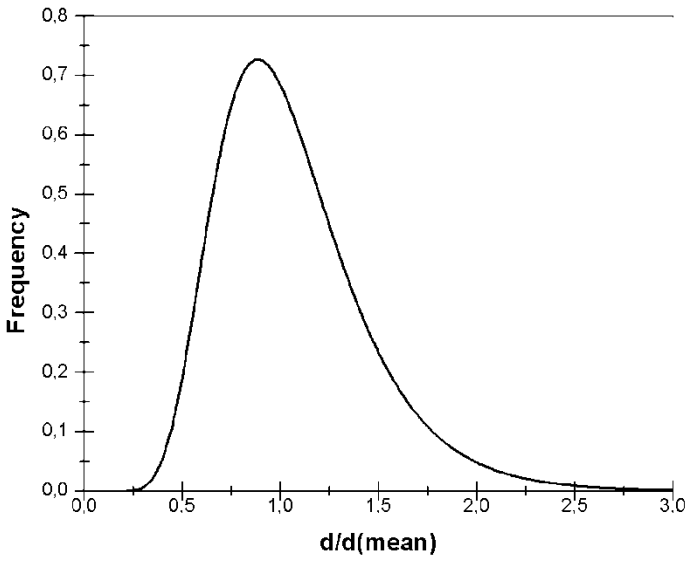
$$D_p = 0.301 D_s \left(\frac{a}{d/2}\right)^4$$



G. Somorjai, *Principles of Surface Chemistry* (Prentice-Hall) (1976)
E. E. Gruber, *J. Appl. Phys.* **38**, 243 (1967)

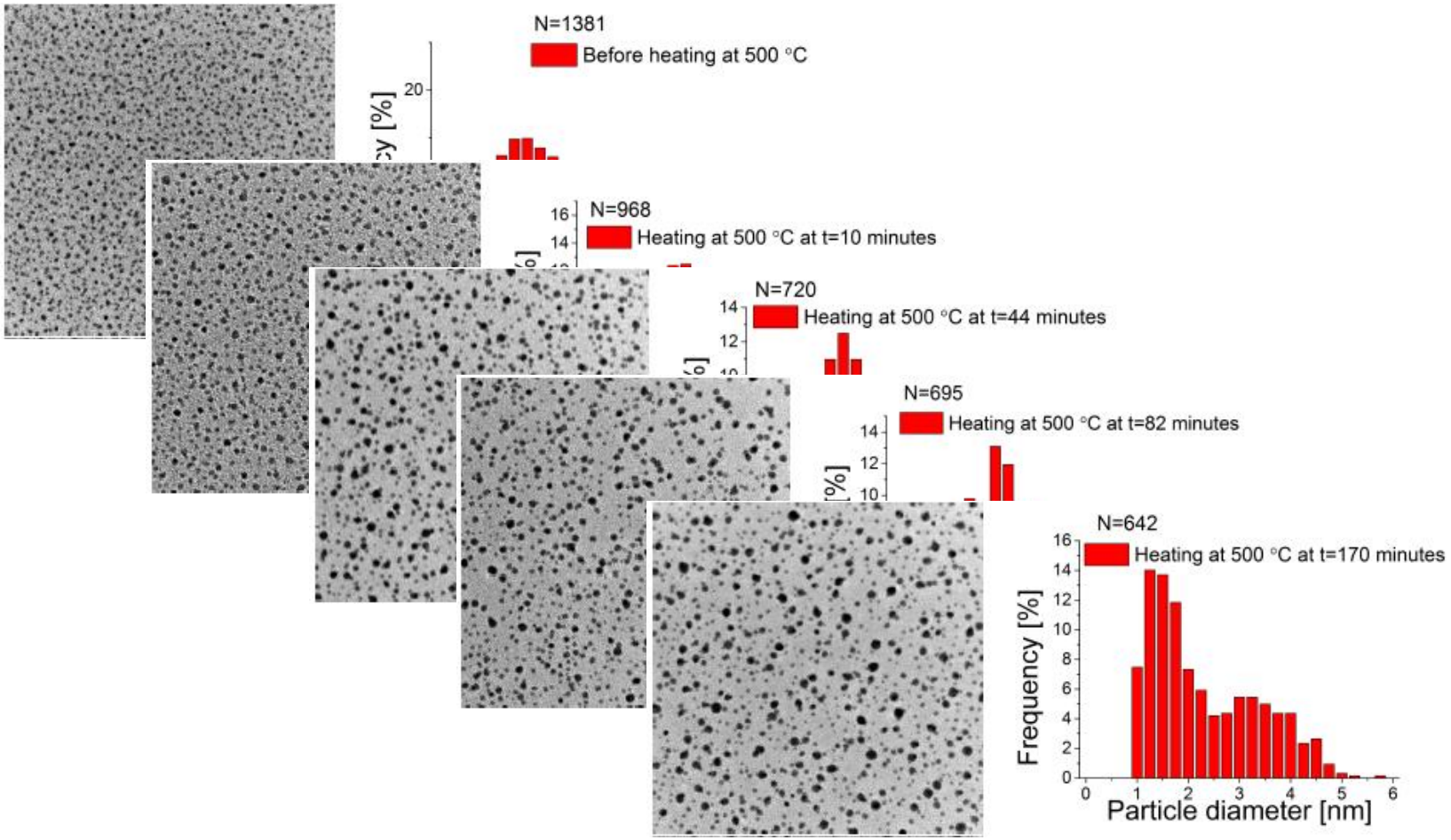
Particle Size Distribution from Particle Migration and Coalescence

- Theoretically, particles sintered by PMC produce a PSD of log-normal shape
- PSDs have a sharp cut-off on the small diameter side and a tail on the large diameter side



$$f_{L-N}(x) = y_0 + \frac{A}{\sqrt{2\pi}wx} \exp \frac{-\left[\ln \frac{x}{x_c}\right]^2}{2w^2}$$

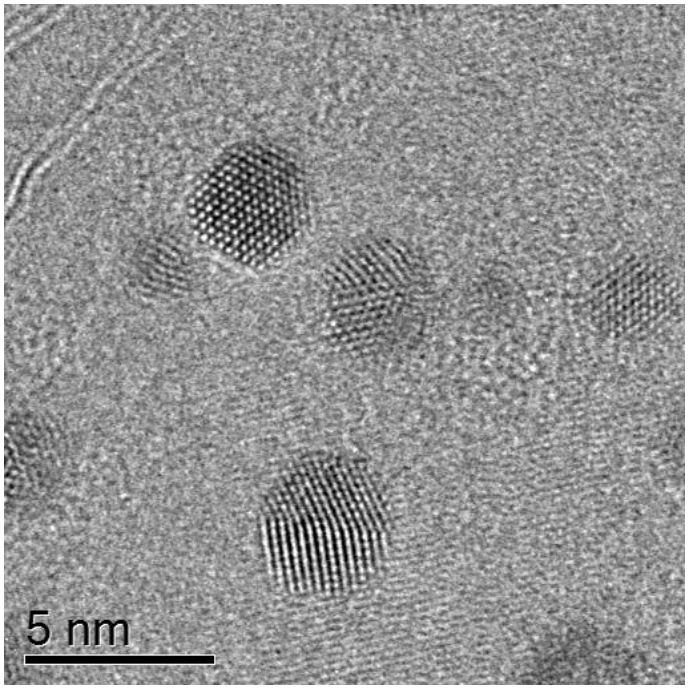
Particle size distribution

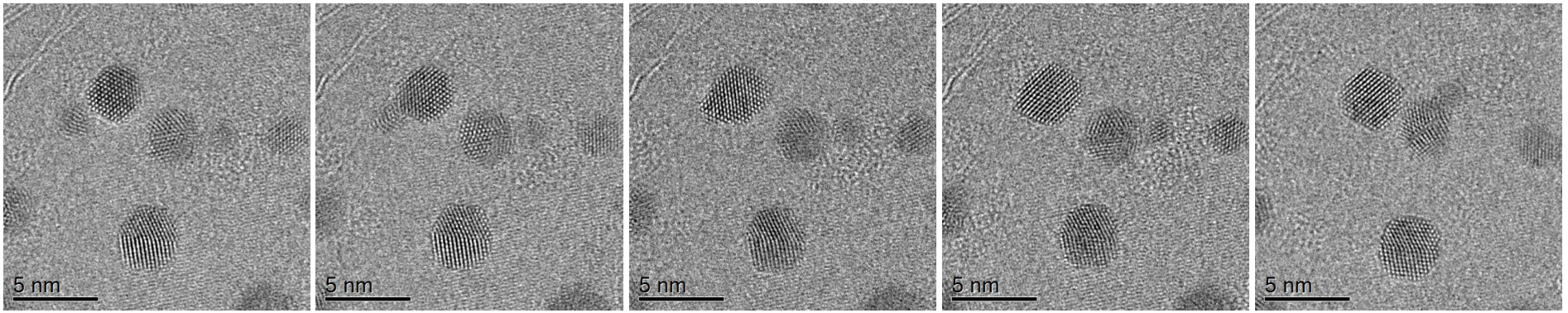


Thanks to Nicolai Støvring and Phillip Brinck Vetter

Au/Graphene

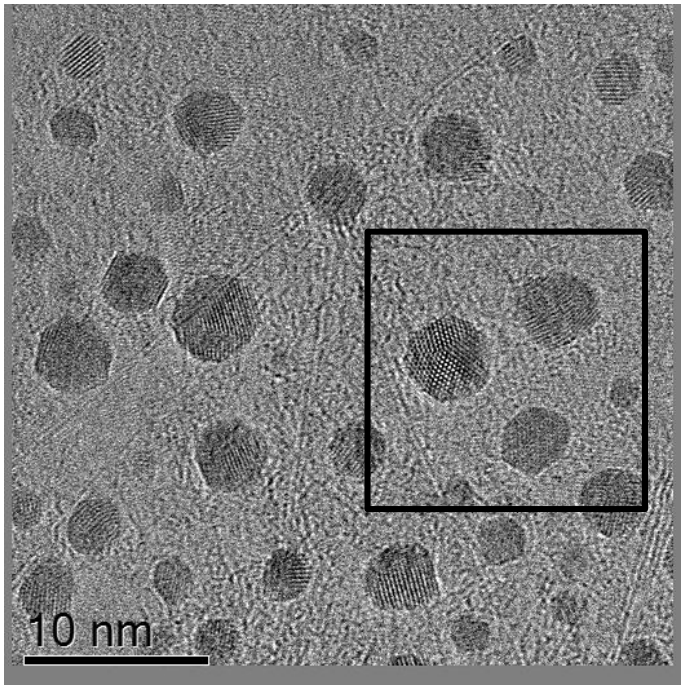
- Ca. 4x real time
- RT, 200Pa H_2
- Particles are more dynamic and move around the support
- Coalescence events are observed, but still occur slowly
- Resulting particles still only slowly retain an equilibrium shape

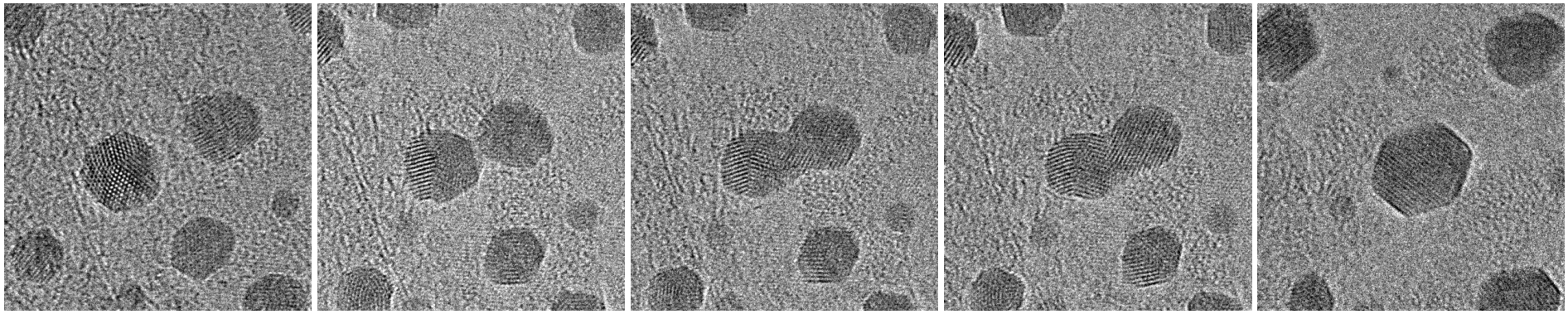




Au/Graphene

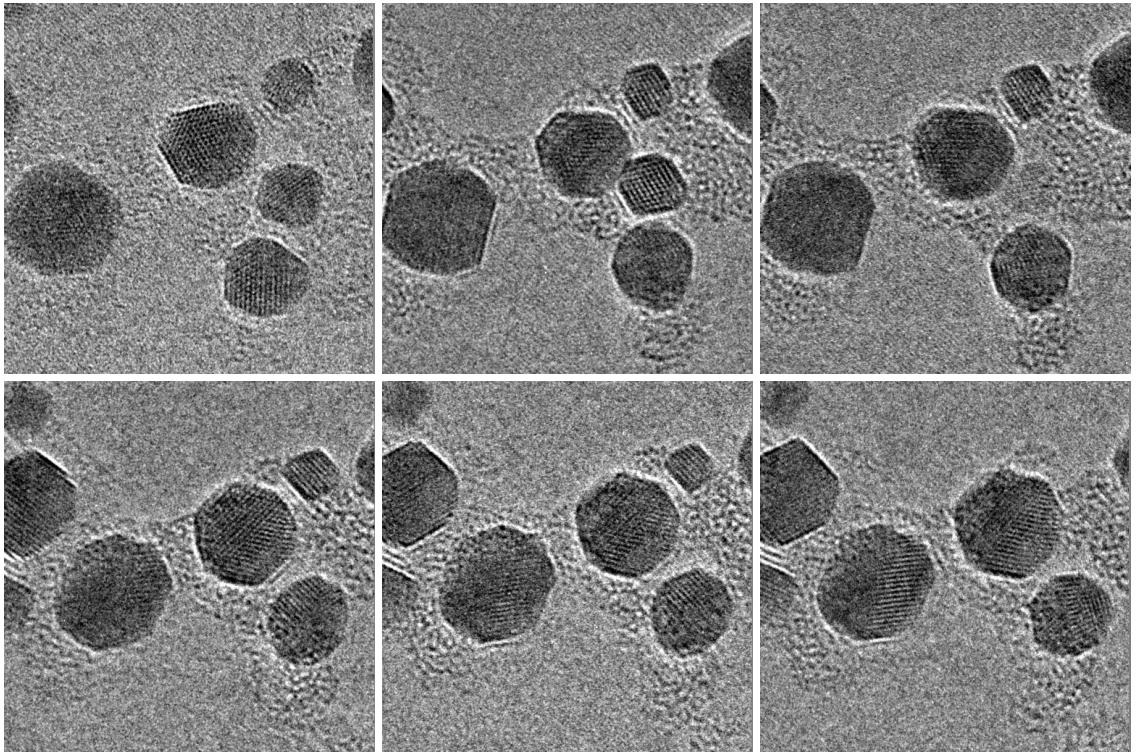
- Ca. 8x real time
- 104°C, 200Pa H_2
- Cross correlation used for image alignment
- At low temperatures, particles wobble around equilibrium positions, but do not tend to migrate long distances
- Particles in close proximity can coalesce into to single particles, but do not readily form single crystalline structures

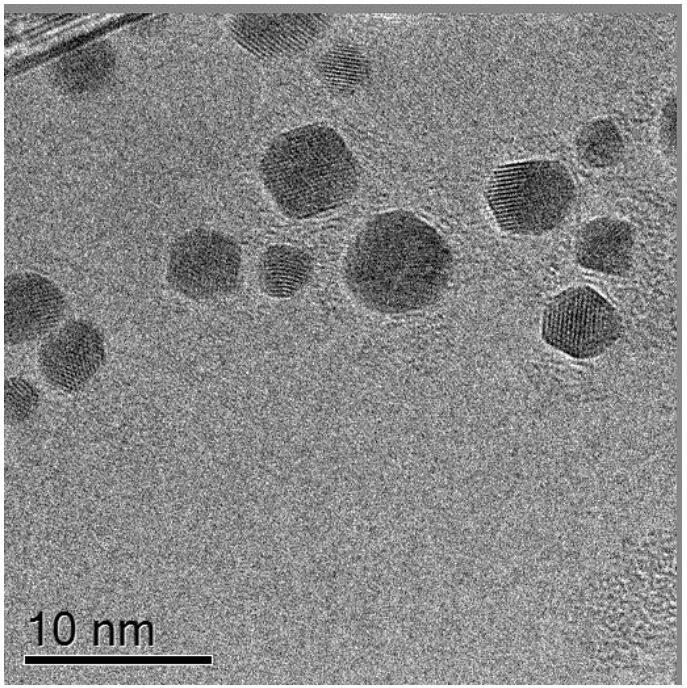




Au/Graphene

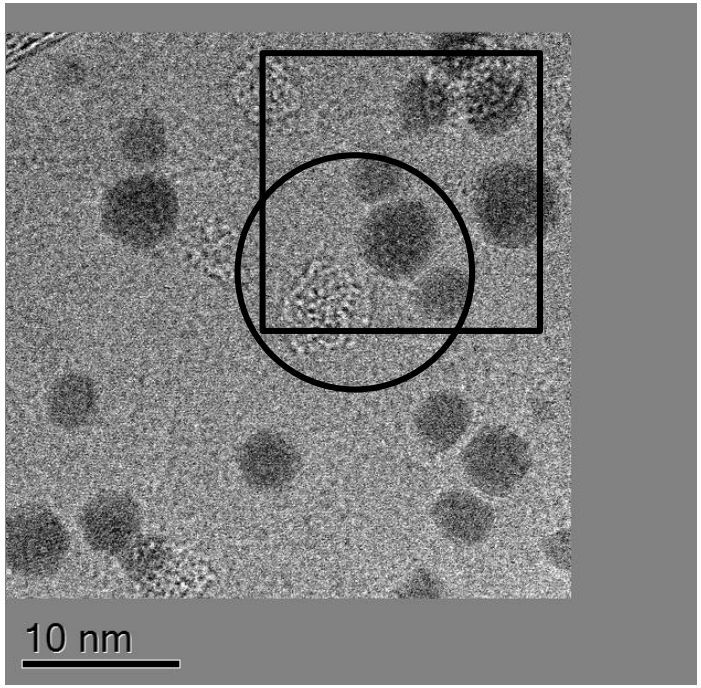
- Ca. 8x real time
- 305°C, 200Pa H_2
- Particles still coalesce readily
- Both initial and final particles appear crystalline at all times.
- Smaller particles are absorbed by larger particles

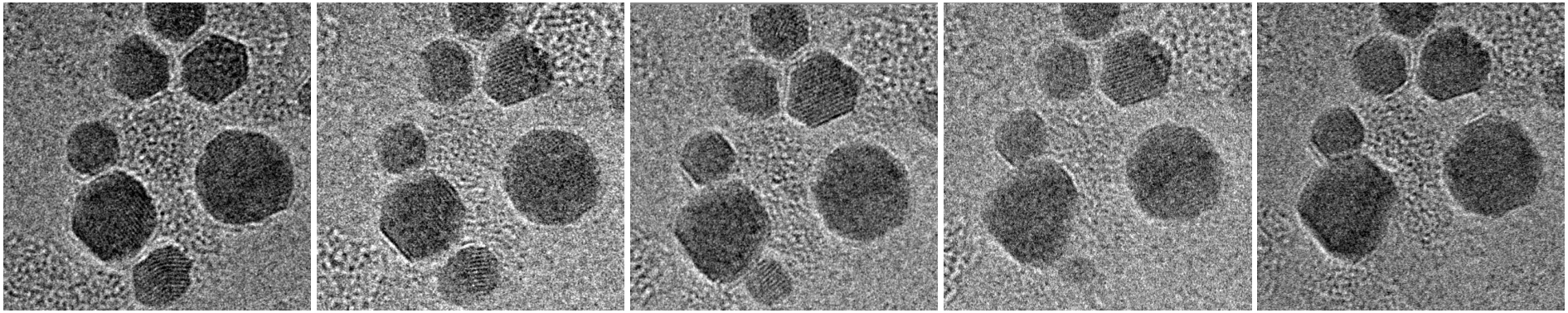




Au/Graphene

- Ca. 8x real time
- 403°C, 200Pa H_2
- Event following both mechanisms occur simultaneously
  - Top: PMC
  - Middle: OR





Conclusions

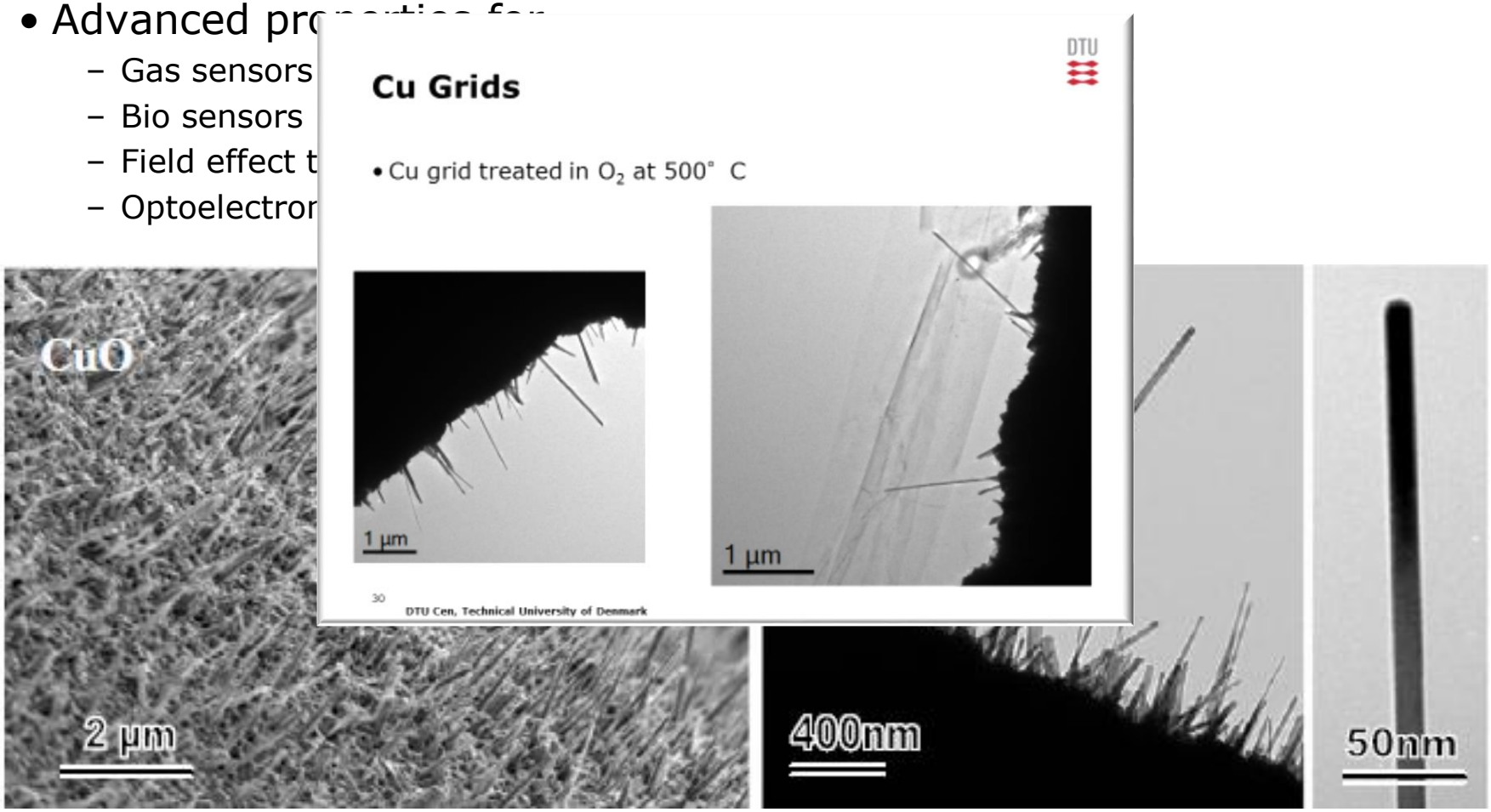
- Nanoparticles are highly mobile in harsh environments
- Multiple sintering mechanisms can work simultaneously
- Mechanisms?
  - Migration and coalescence
  - Ostwald ripening
  - Suction of matter when particles are in close proximity
- Nanoparticles can merge as crystalline entities
- Mass is rapidly distributed throughout resulting particles

Copper oxide nanowires

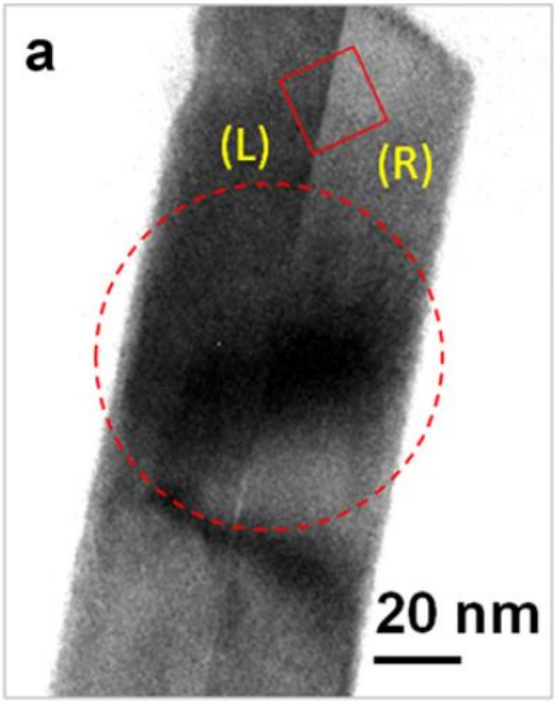
ANISOTROPIC OXIDATION

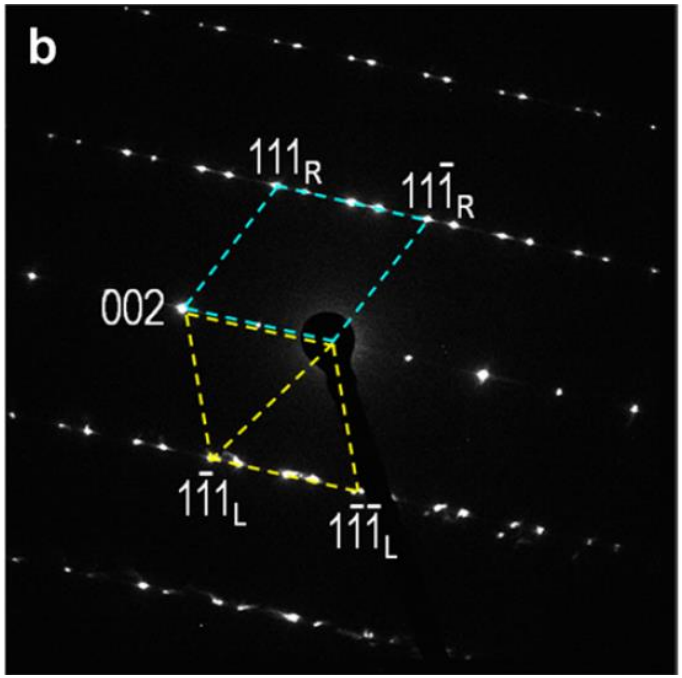
Copper Oxide Nanowires

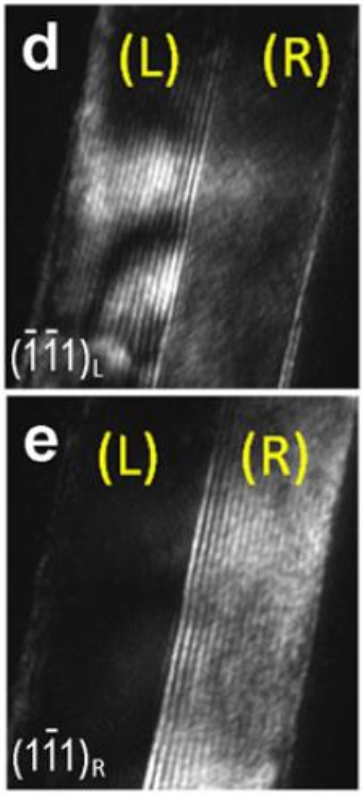
- Advanced pr
  - Gas sensors
  - Bio sensors
  - Field effect t
  - Optoelectron



Post Mortem characterization of CuO NWs





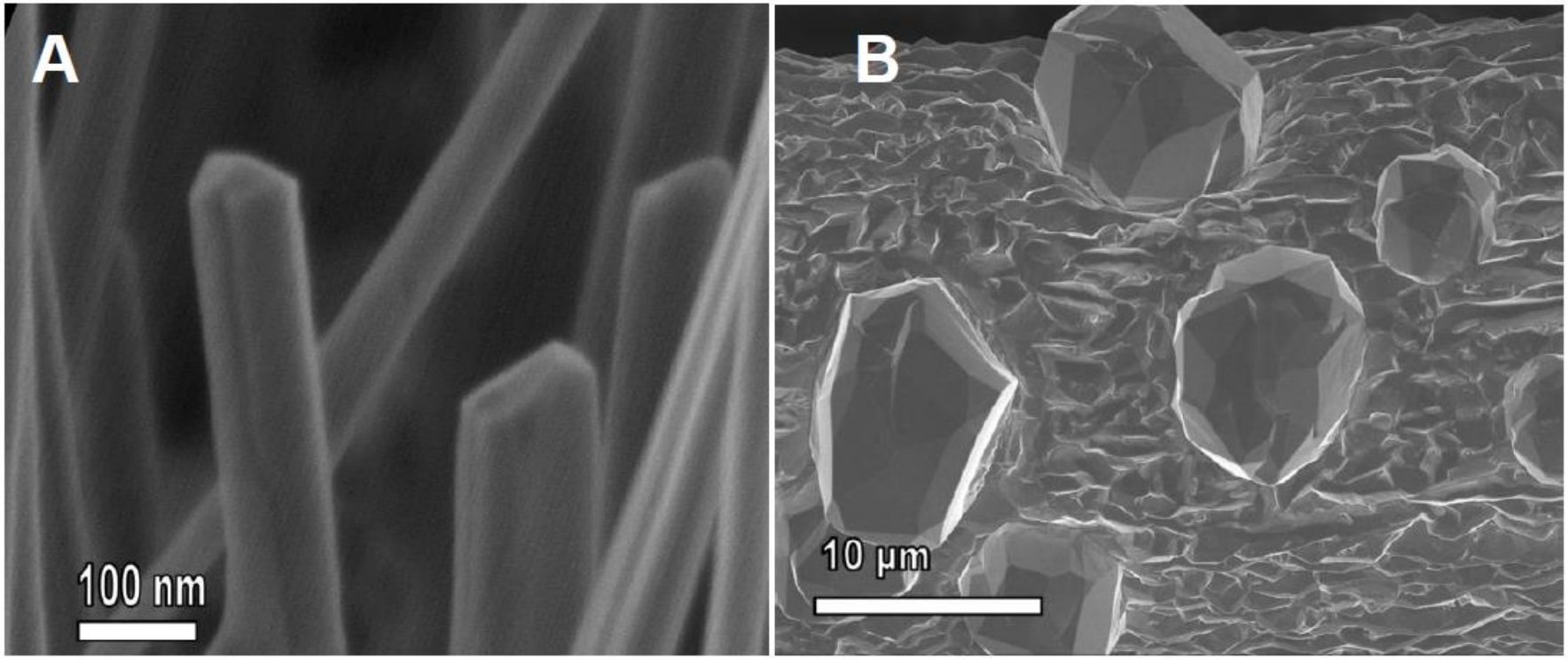


…but how do they grow?

S. Rackauskas, JBW *et al.*, *Nano Letters* 14, 5810 (2014)

Ex situ Cu oxidation

- 400˚C

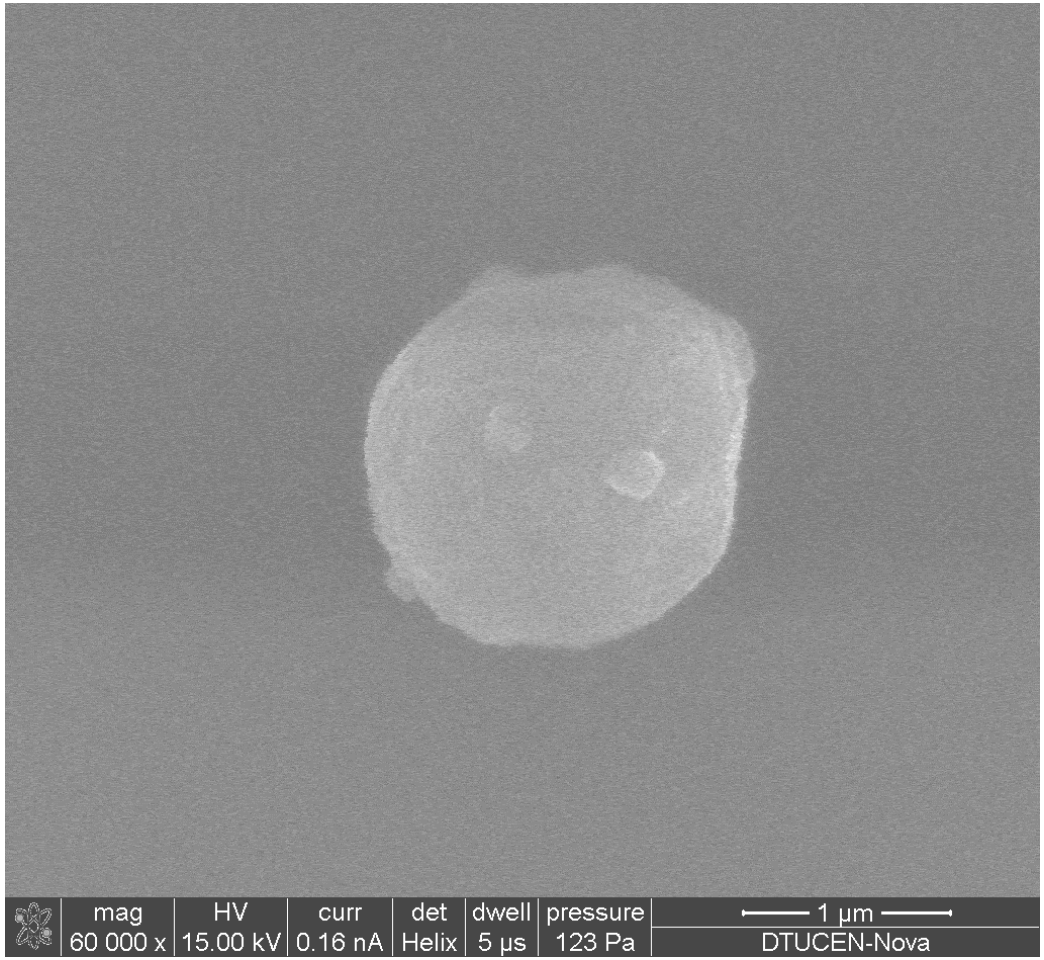


Ambient air

20 Pa O_2

Oxidation of Cu particles in the SEM

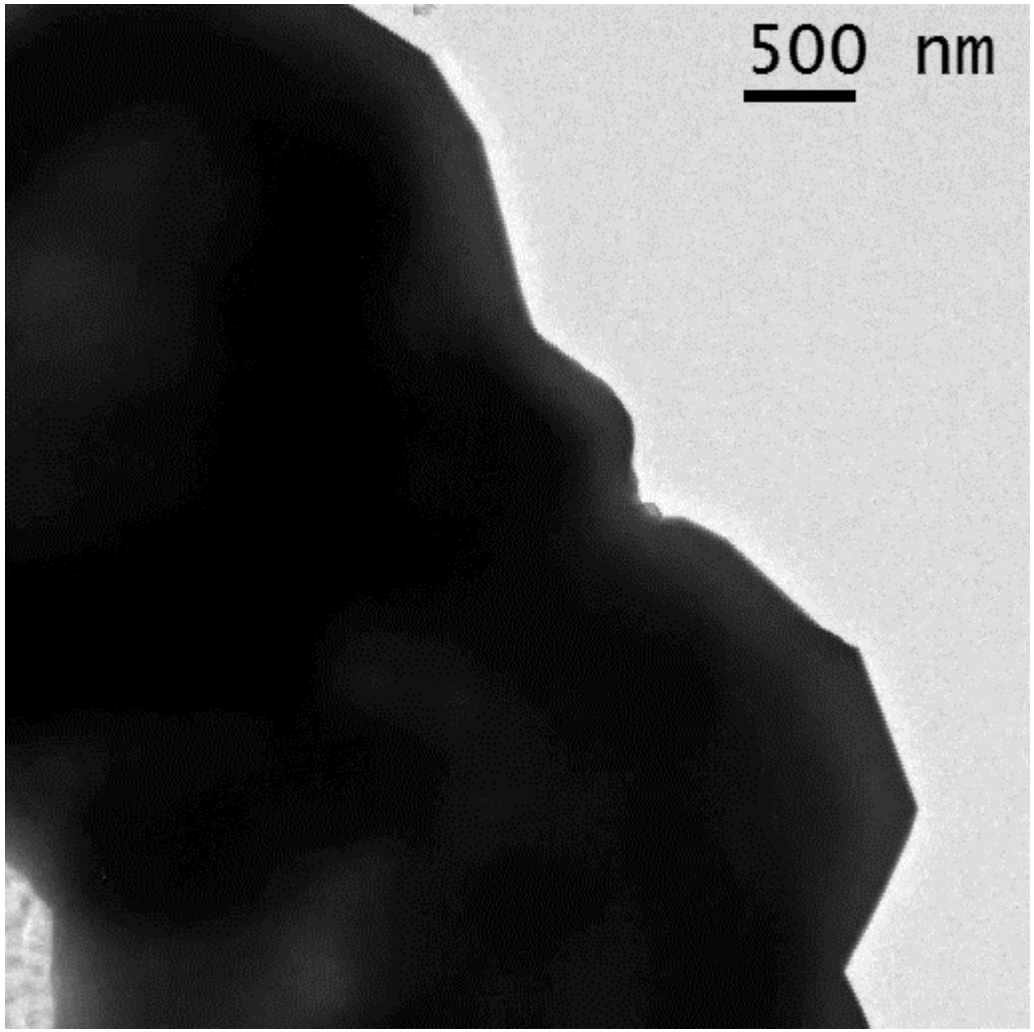
- **Temperature:** 450°C
- **Atmosphere:** Oxygen
- **Video:** 100 x realtime



M. M. Kone, M. Ahmed, and A. Fuller.

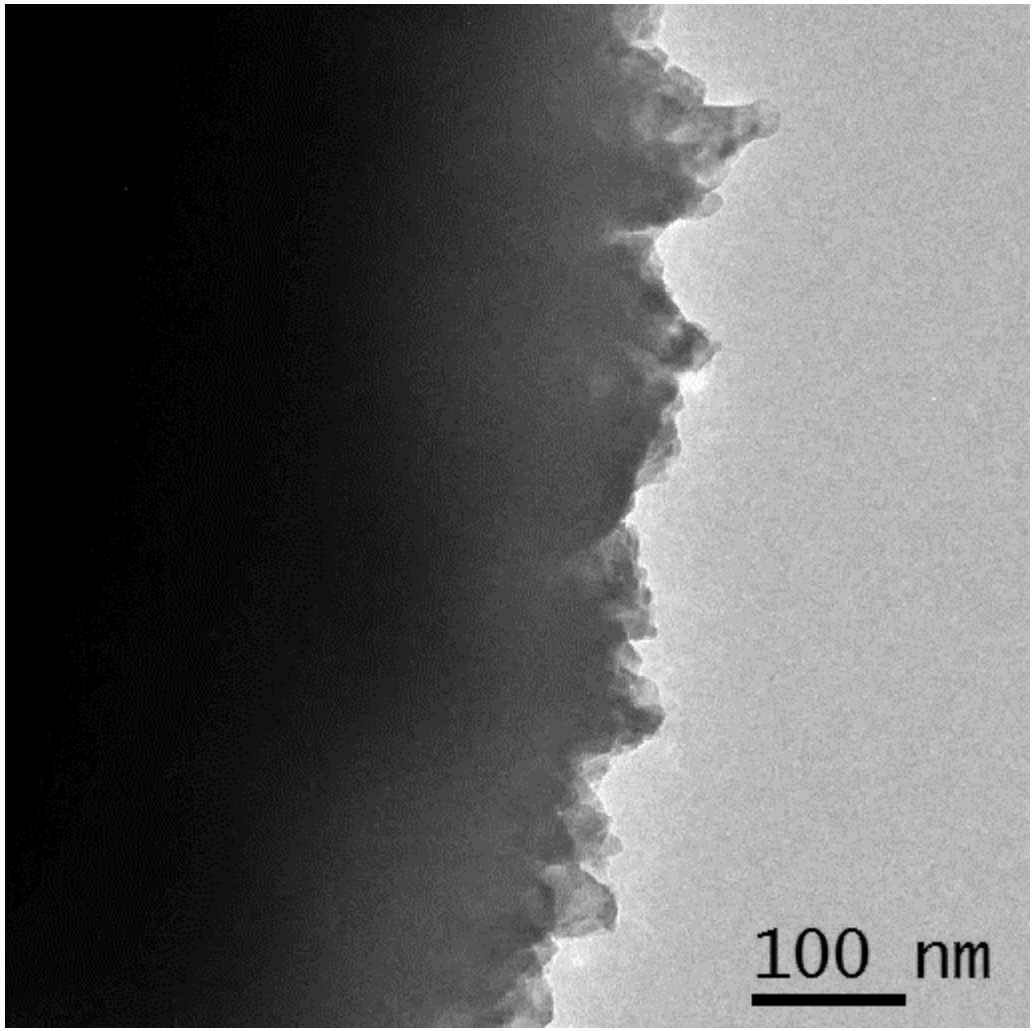
Oxidation of Copper

- Cu particle (5μm)
- 310Pa O_2
- Heating to 350°C



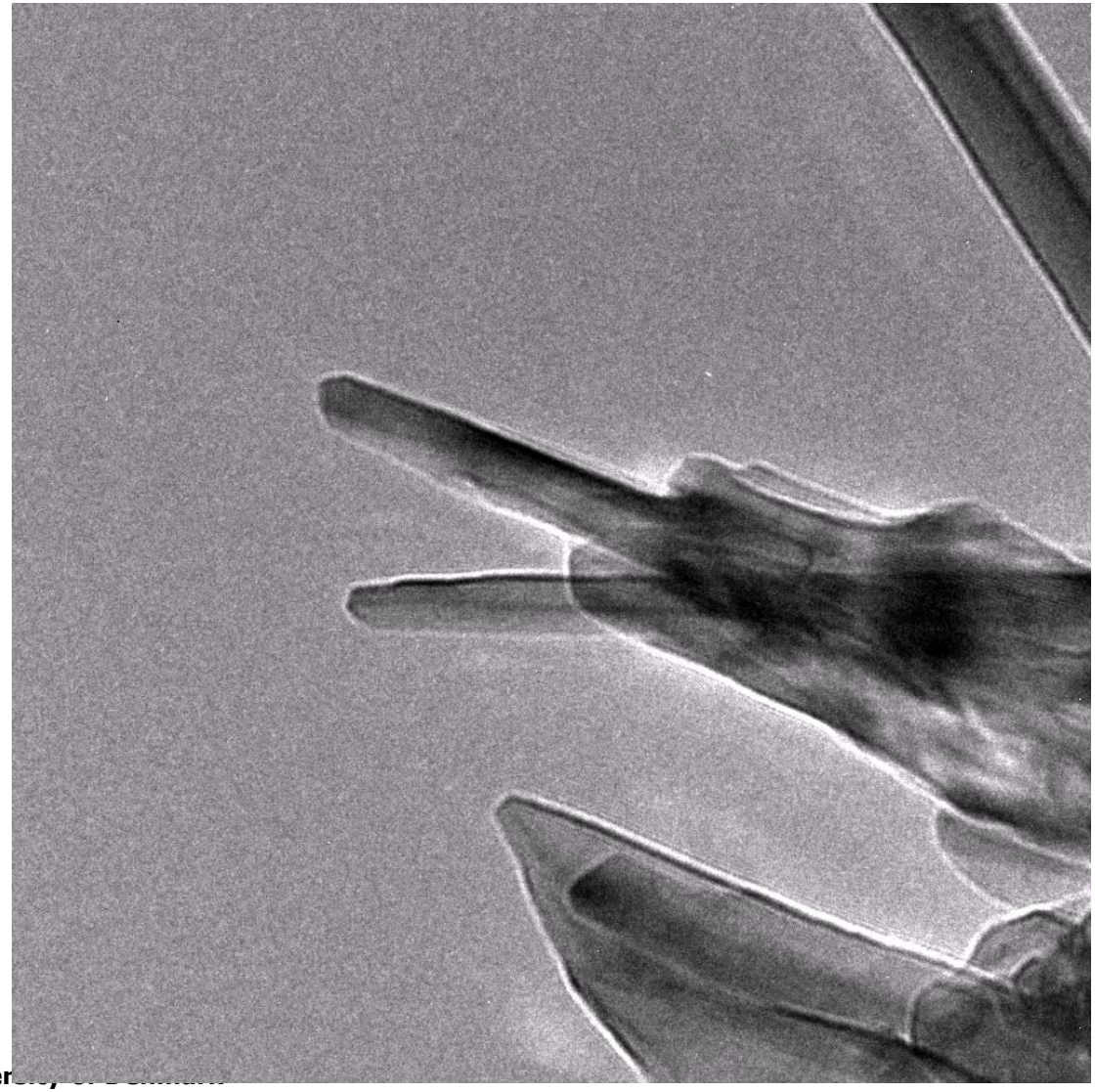
Oxidation of Copper

- Cu particle (5μm)
- 680Pa O_2
- Heating to 350°C



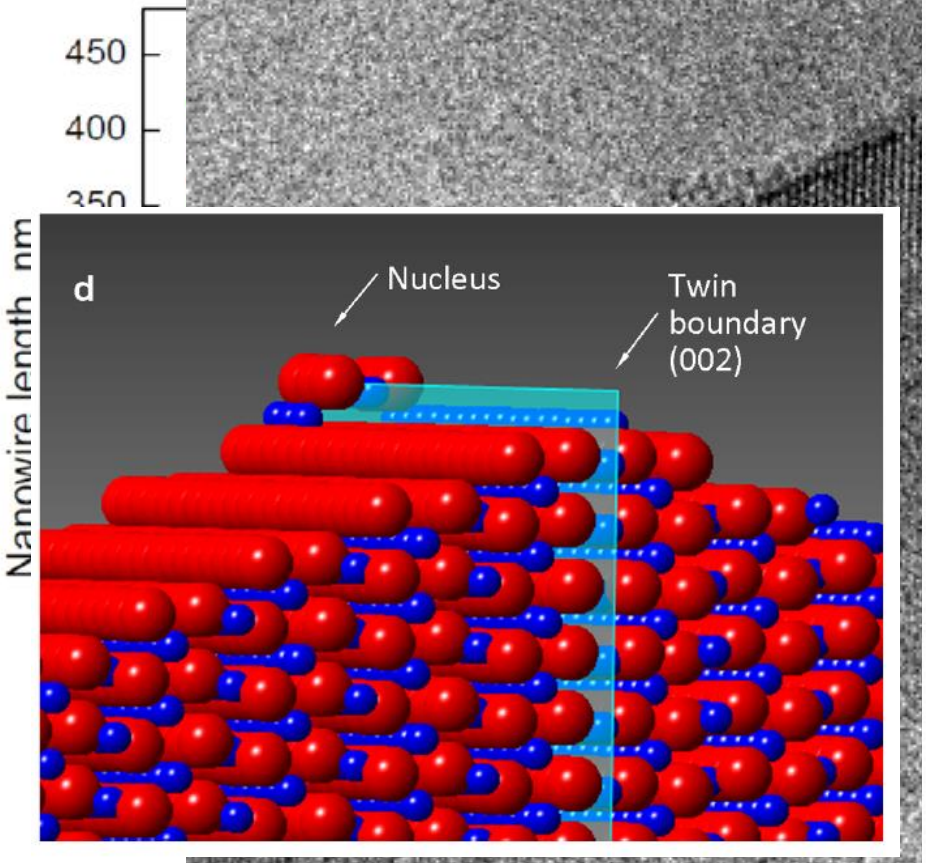
Lowmag movie of growth

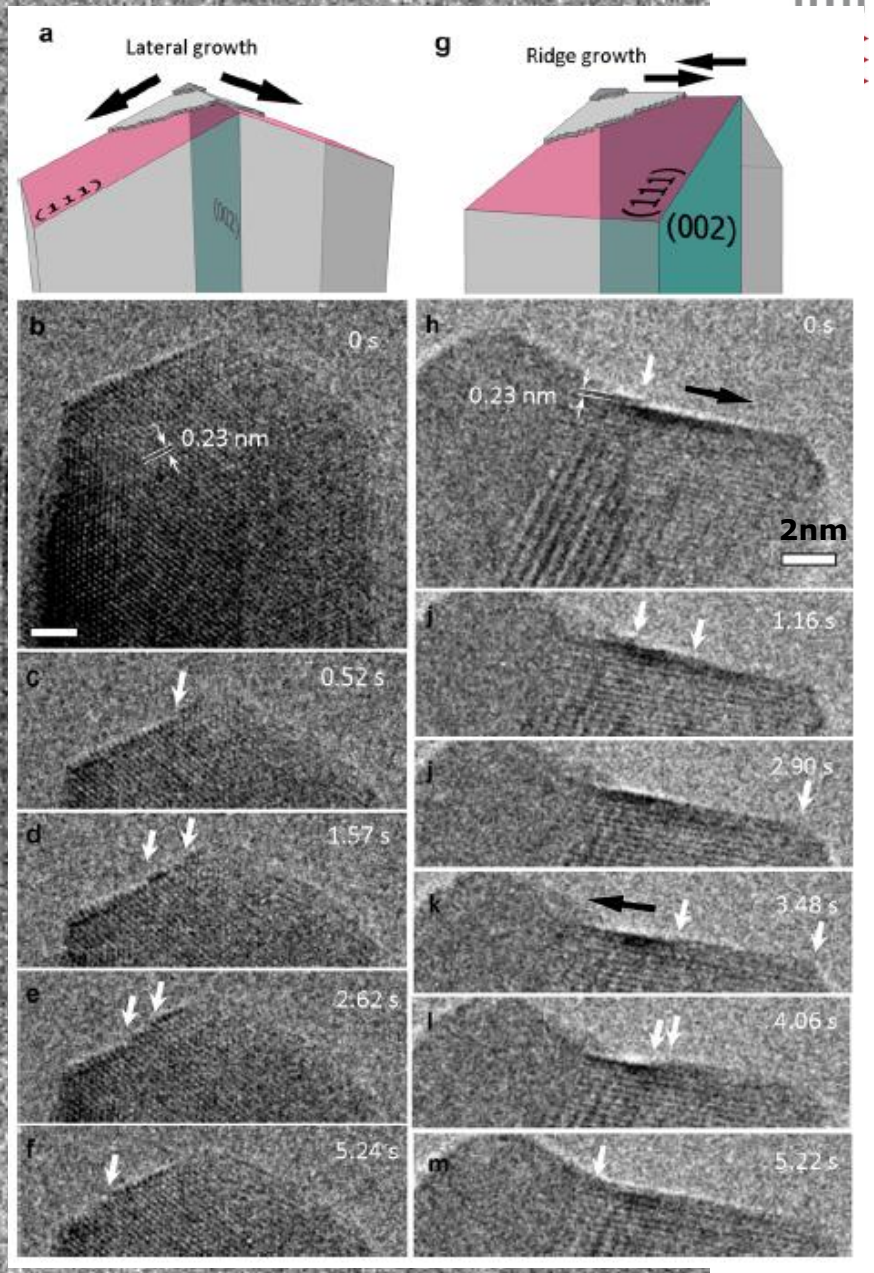
- T=370°C
- P=680Pa



Ho

- 68





S. Rackauskas, JBW *et al.*, *Nano Letters* 14, 5810 (2014)

Graphene(?)

PLANAR GROWTH OF CARBON LAYERS

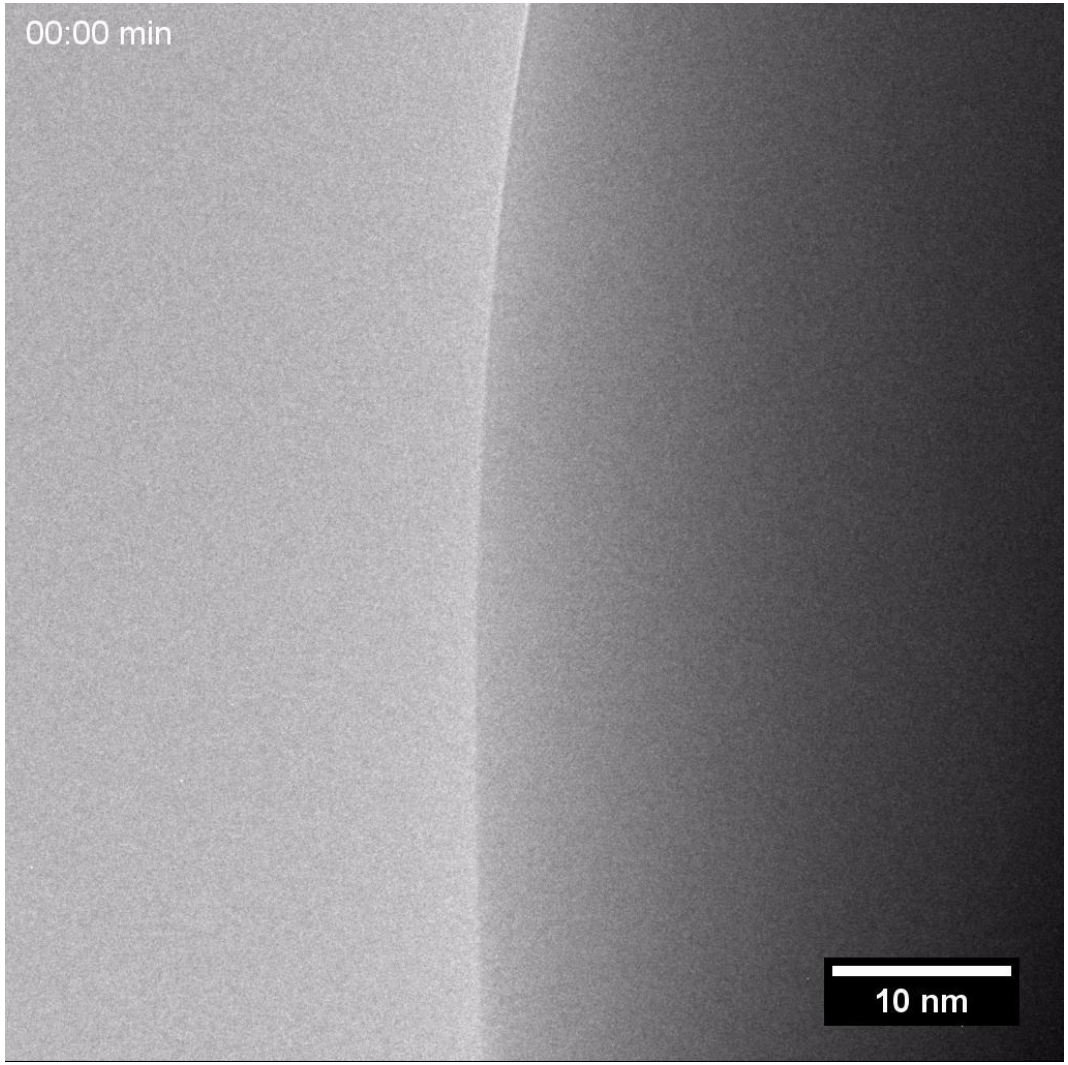
In situ Carbon Growth on Ni

- T=650°C in 120Pa H_2
- Leaking in 3×10^{-2}Pa C_2H_2

- 0.61s between each image

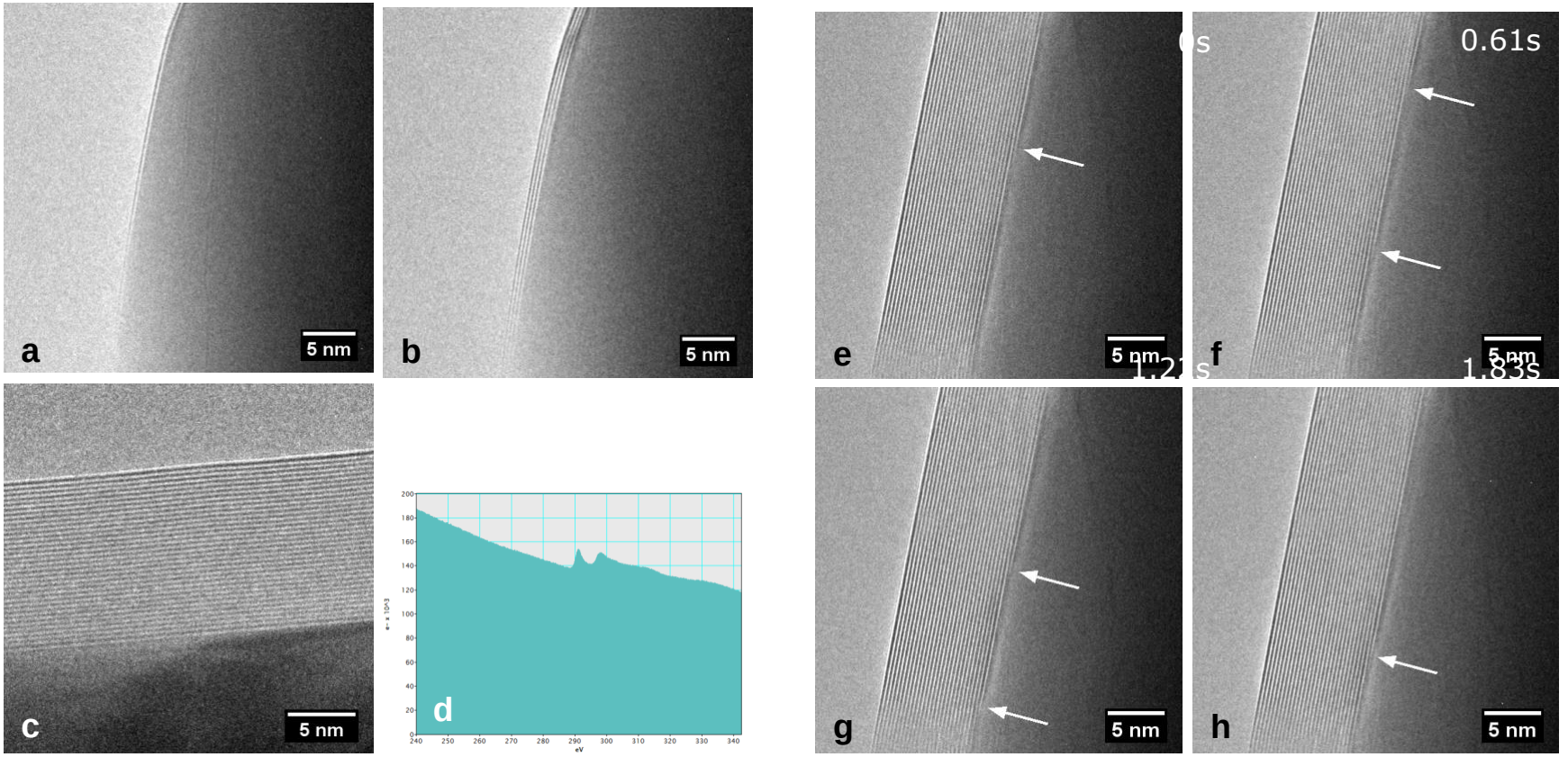
→Quick initial growth shortly after flowing acetylene

→Growth of the layers and the growth front can be followed



J. Kling, T. W. Hansen, JBW, Carbon **99**, 261 (2016)

In situ Carbon Growth on Ni



ETEM experiment; T=650°C; 120Pa H_2/3×10^{-2}Pa C_2H_2

→Well aligned carbon layers at the Ni surface (a-c)

→EELS shows C edge for graphitic structure (d)

→Several growth fronts observed (e-h)

J. Kling, T. W. Hansen, JBW, Carbon **99**, 261 (2016)

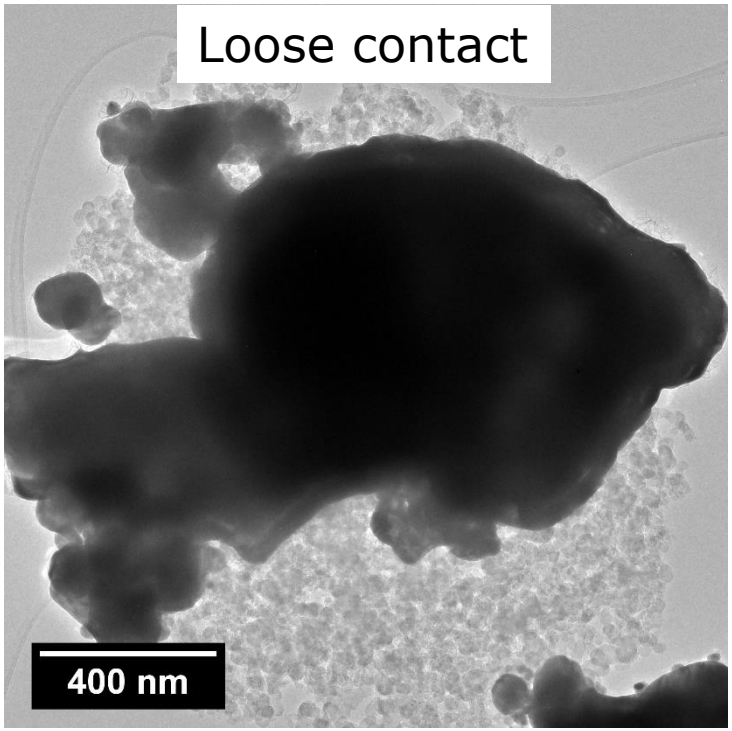
Soot oxidation by Ag

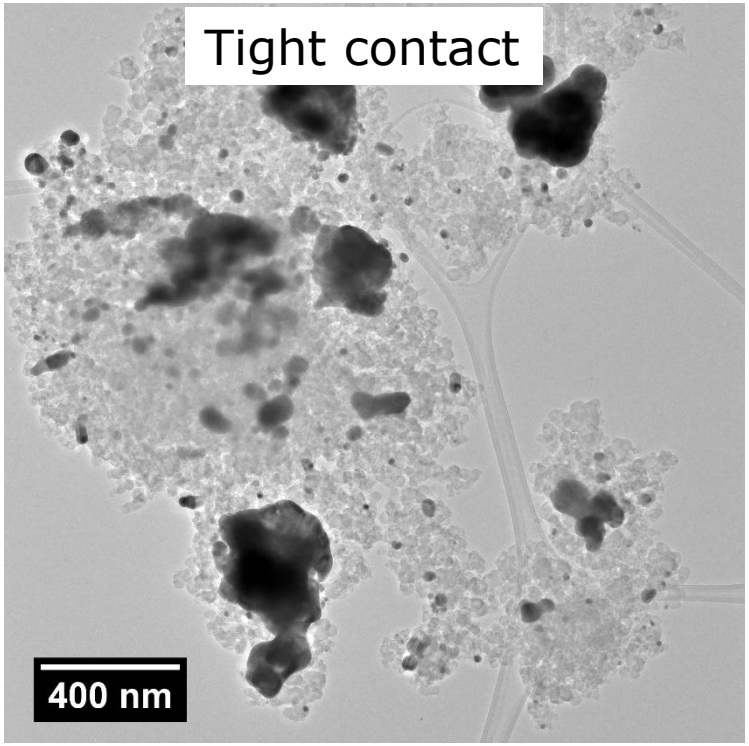
WATCHING THE REACTION

Soot oxidation by Ag catalyst

- Remove soot particles in exhaust of diesel engines by filters for a cleaner and healthier environment

- Low temperature regeneration of filters to reduce fuel consumption

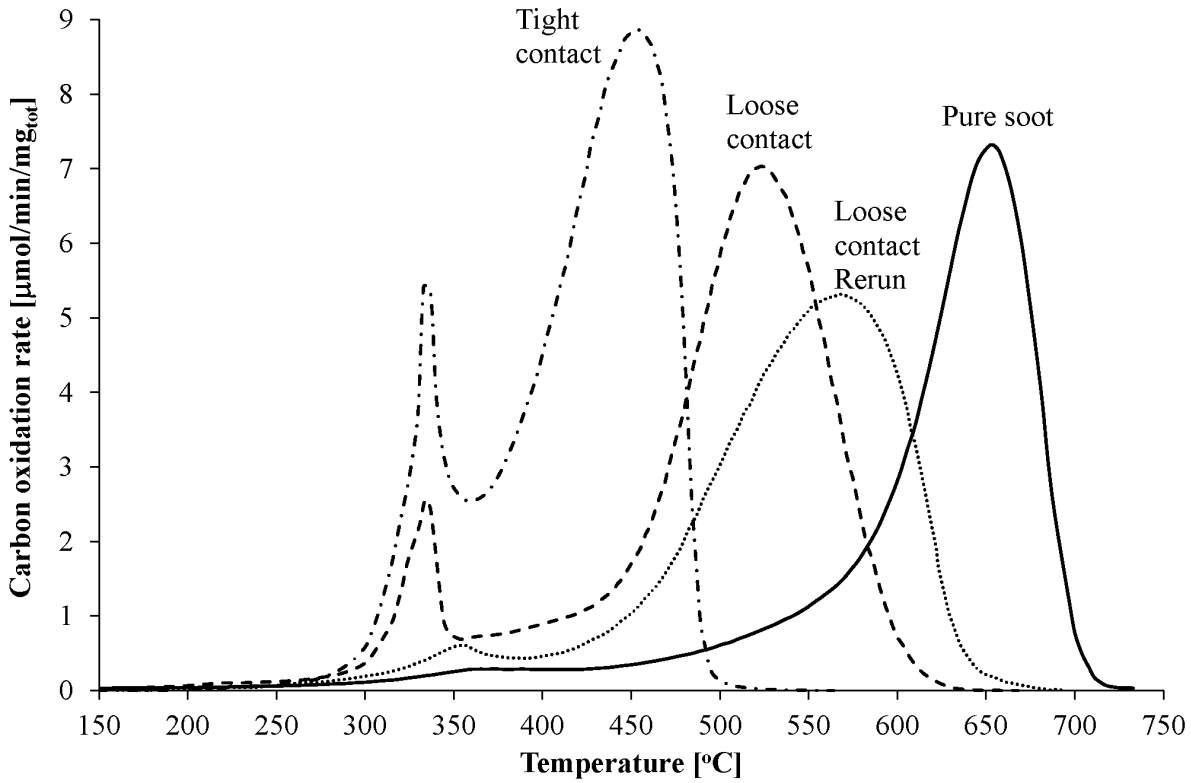




D. Gardini, JBW et al. Appl. Catal. B 183, 28 (2016)

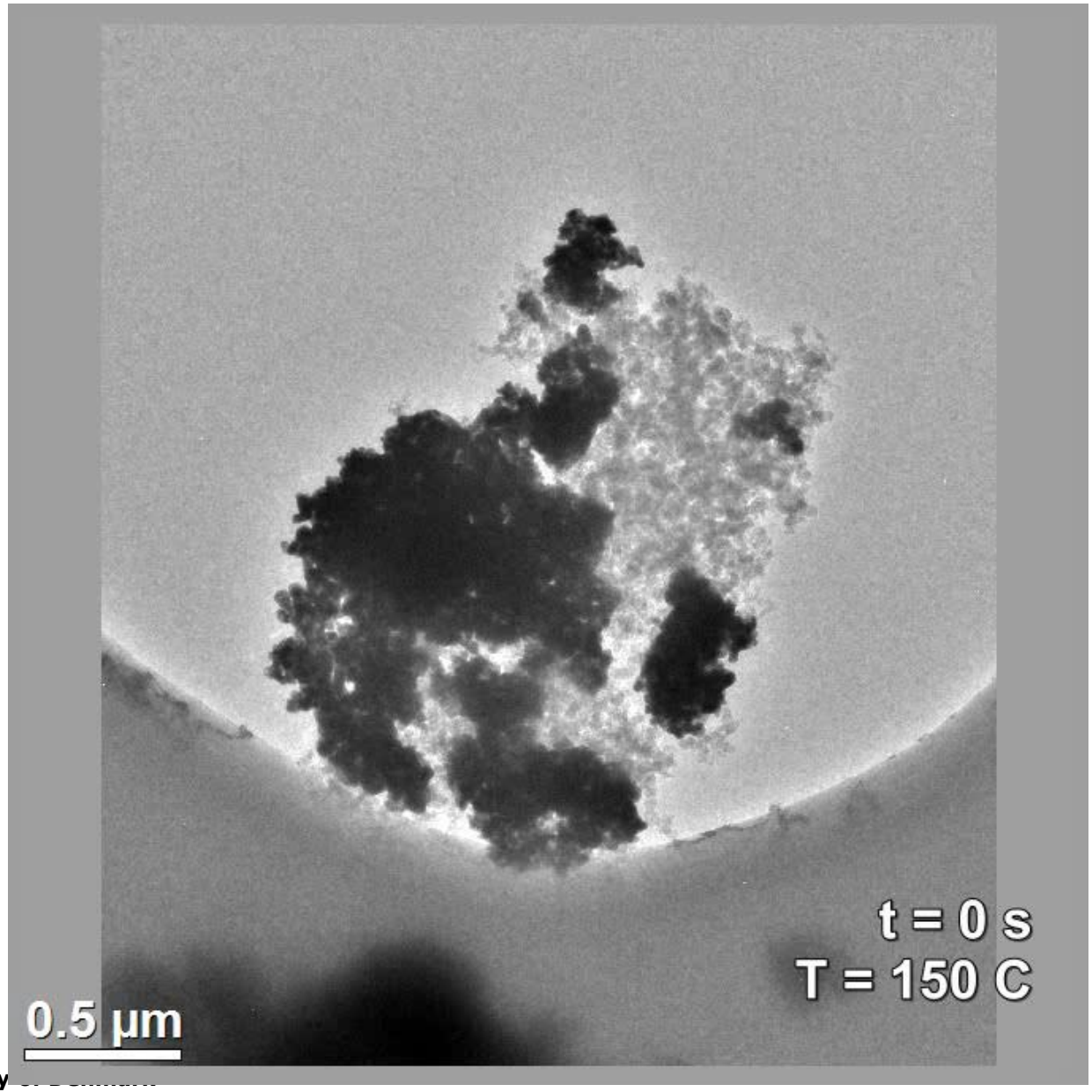
Silver Catalyst for Low Temperature Soot Oxidation

- Soot:silver= 1:5 wt:wt,
- Heating ramp = 11°C/min,
- 1 NL/min, 10.2 vol% O_2 in N_2.



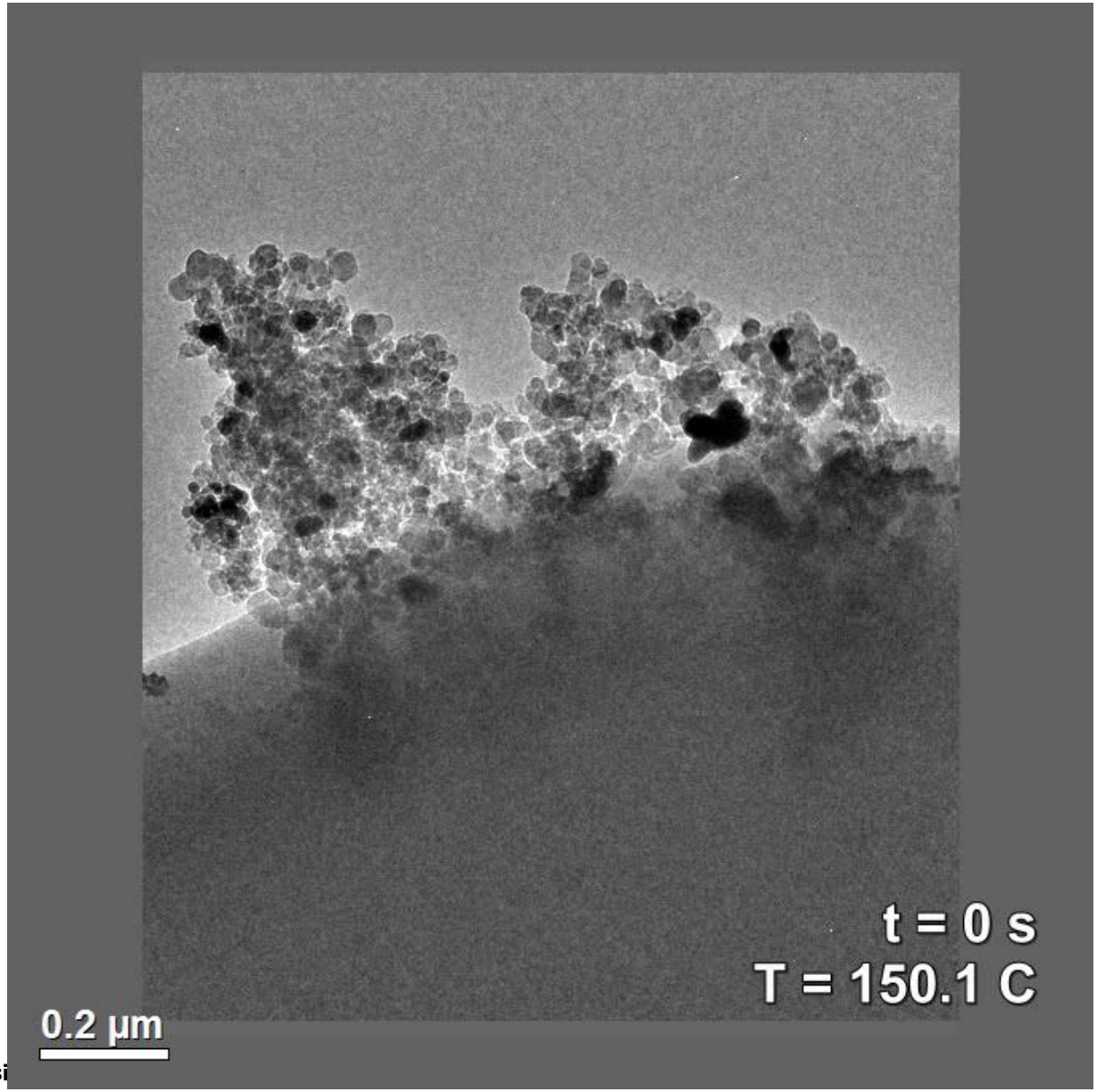
Loose contact

- P=300 Pa O_2



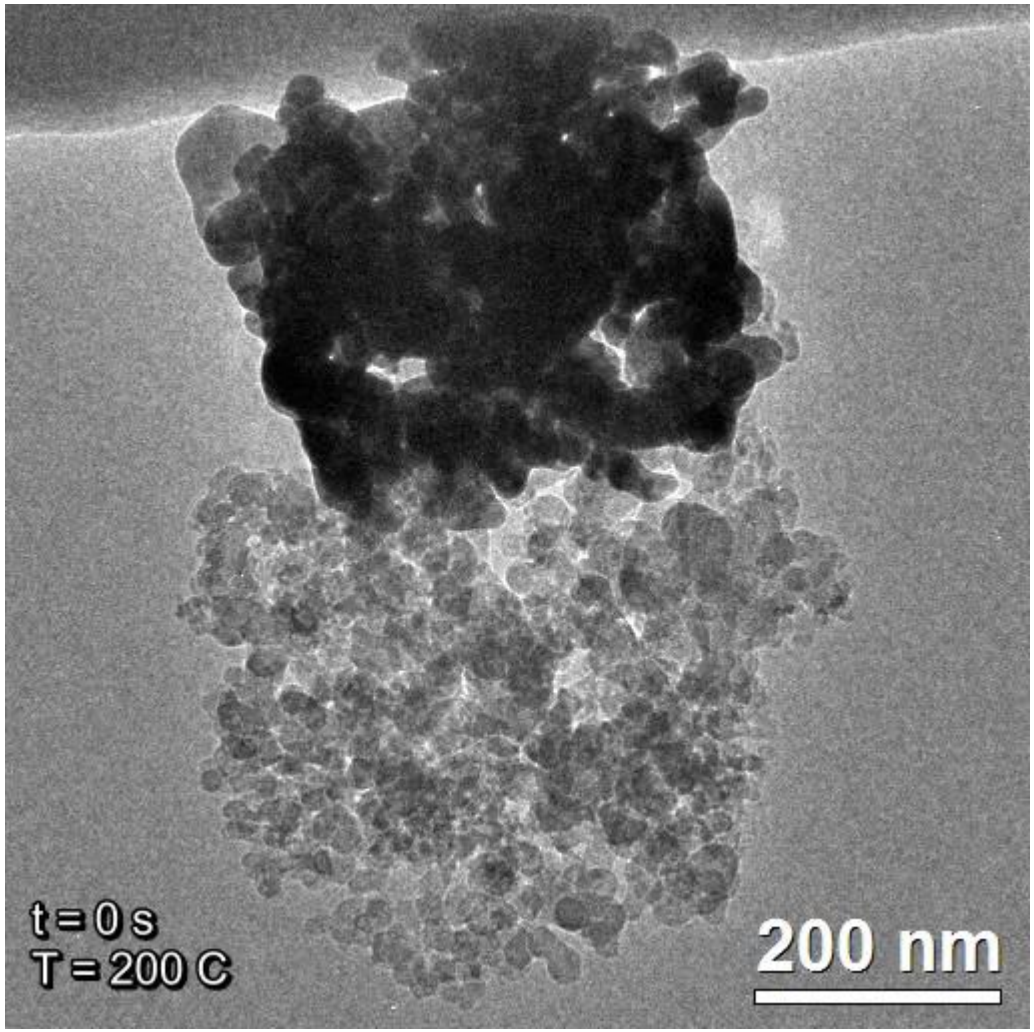
Tight contact

- P=300 Pa O_2



Silver mobility on loose contact

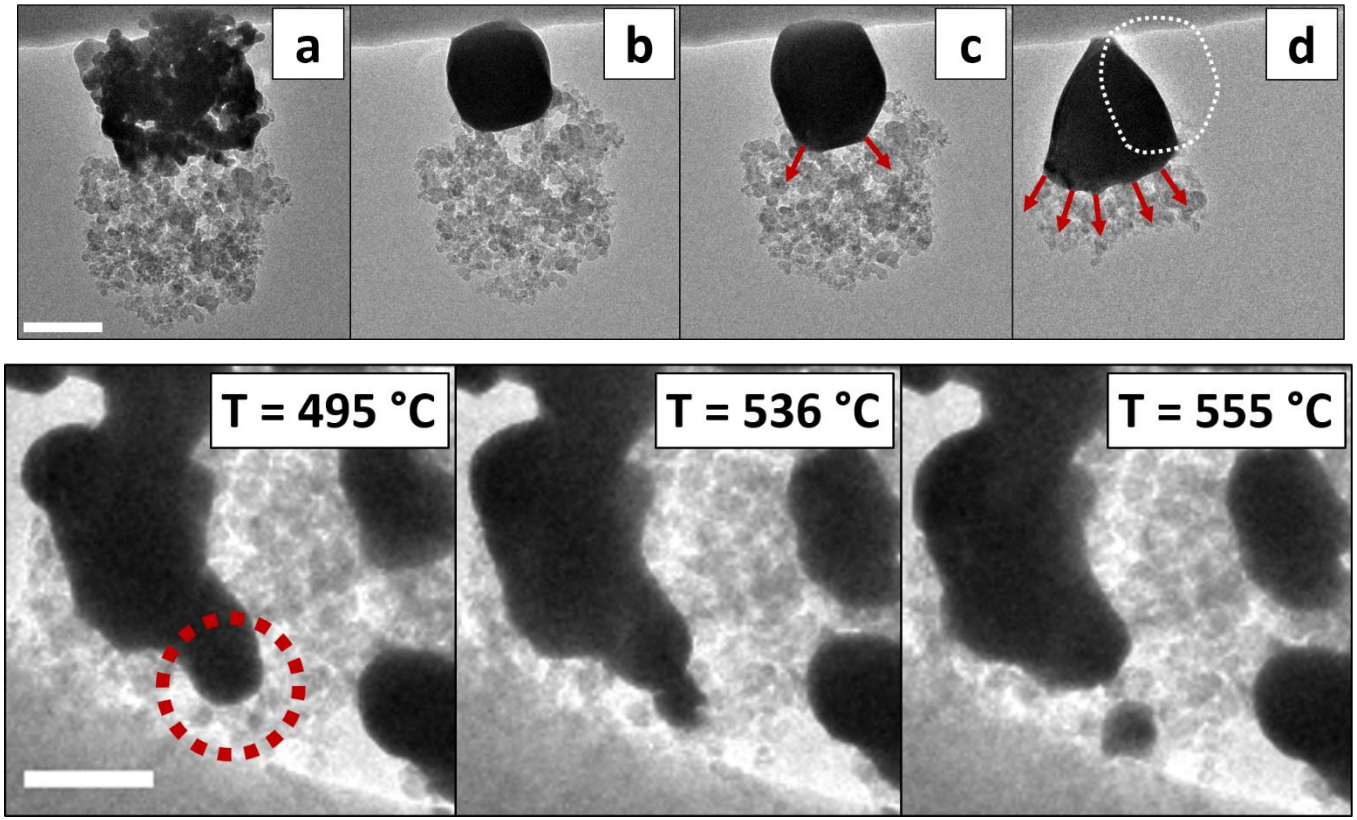
- P=300 Pa O_2
- Ag/soot interface increases during oxidation



D. Gardini, JBW et al. Appl. Catal. B 183, 28 (2016)

Silver mobility on loose contact

- Ag/soot interface increases during oxidation
- Ag detaches

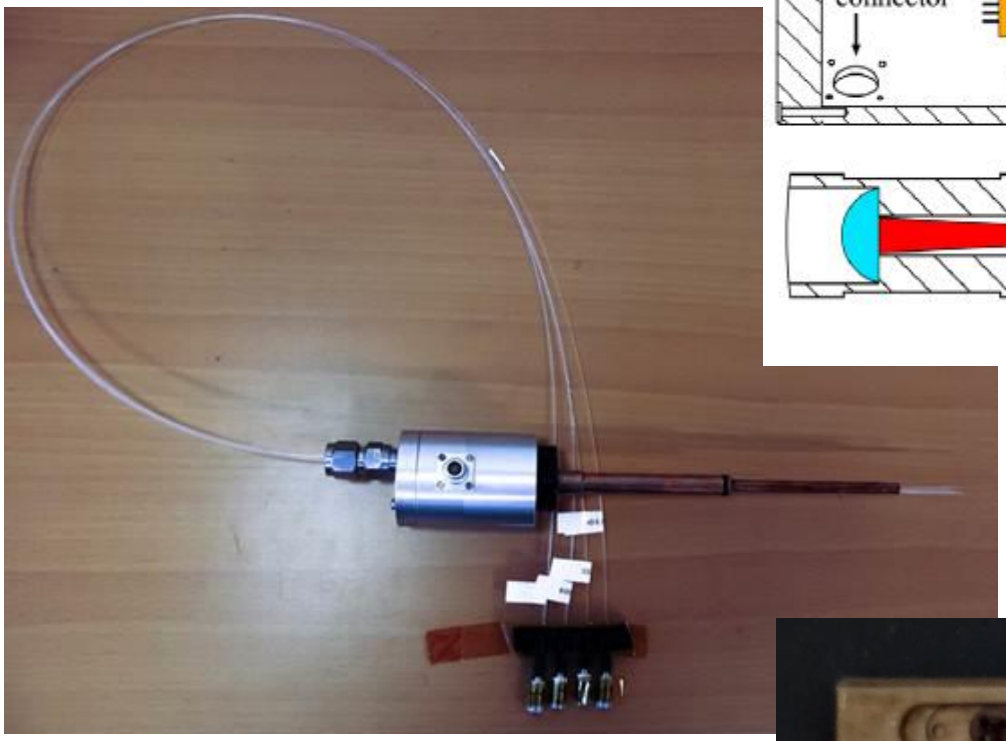


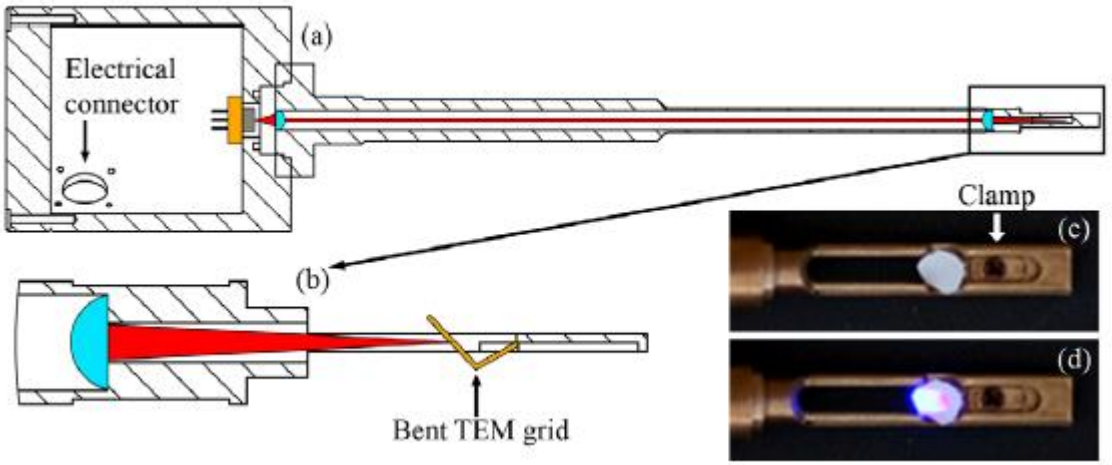
D. Gardini, JBW et al. Appl. Catal. B 183, 28 (2016)

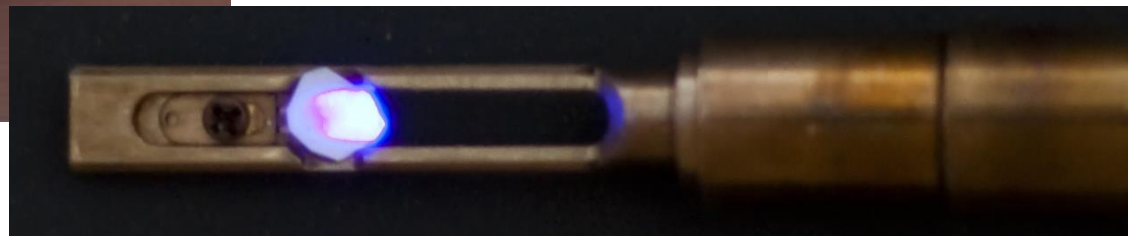
Prospects for Photocatalysis studies

SHINING LIGHT ON THE ETEM

Putting Light in the Microscope



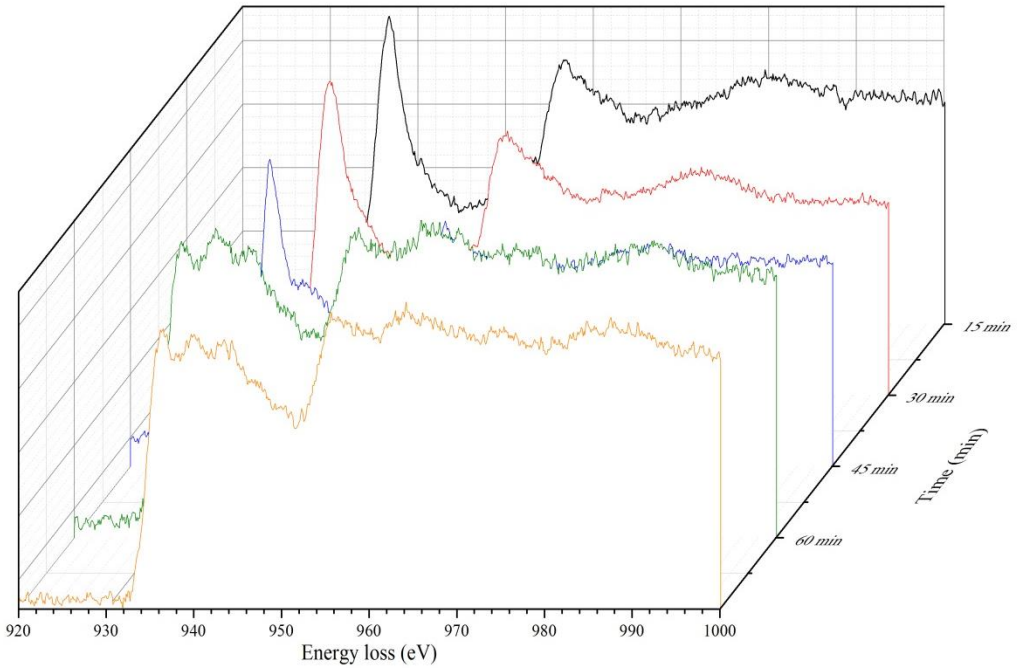


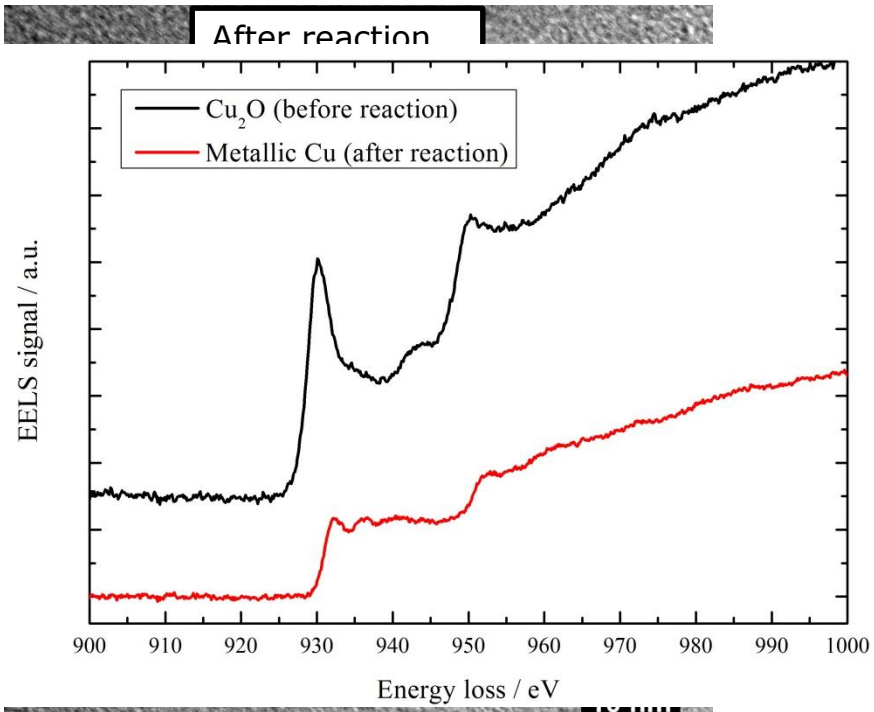


F. Cavalca, JBW et al. Nanotechnology **23**, 075705 (2012)

In situ Cu_2O photocorrosion

- Cu_2O is a photocatalyst for water splitting under visible light illumination.
- It undergoes photodegradation in an aqueous environment.
- The $L_{2,3}$ thresholds («white-lines») reflect the oxydation state of Cu
- The reaction is performed in absence of the electron beam
- 300 Pa H_2O with λ=405nm





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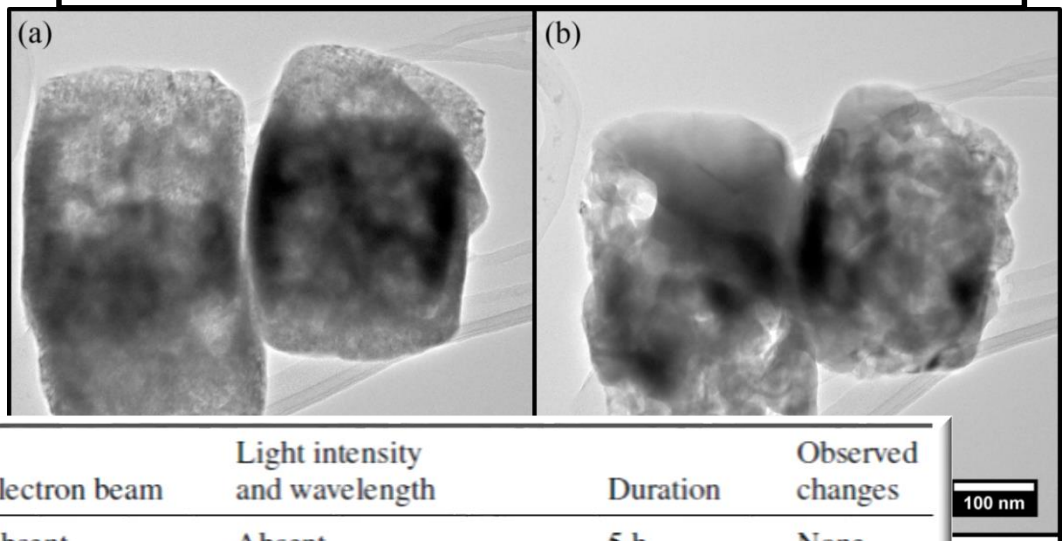
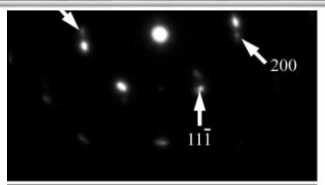
Cu_2O photocatalyst for Water splitting

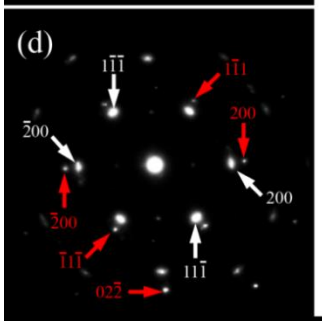
- Cu_2O nanocubes are stable in the electron beam at 300 kV in high vacuum
- Reduction from Cuprous Oxide (Cu_2O) to metallic Cu in presence of water vapor
- V
  - EELS spectra of Cu_2O and metallic Cu
  - The $L_{2,3}$ white-lines ratio reflect the chemical state of Cu

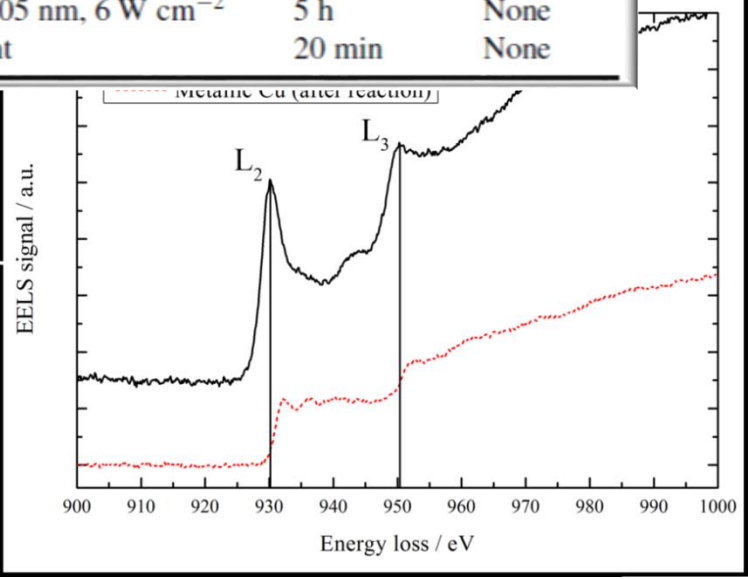
Degradation of Cu_2O nanocubes in H_2O (5 mbar) under visible light illumination (405 nm) for 3 hours.



Experiment	Gas	Pressure (mbar)	Electron beam	Light intensity and wavelength	Duration	Observed changes
1	H_2O vapor	3	Absent	Absent	5 h	None
2	Vacuum	10^{-6}	Absent	$\lambda = 405$ nm, 6 W cm^{-2}	5 h	None
3	Vacuum	10^{-6}	~100 MW cm^{-2}	Absent	20 min	None







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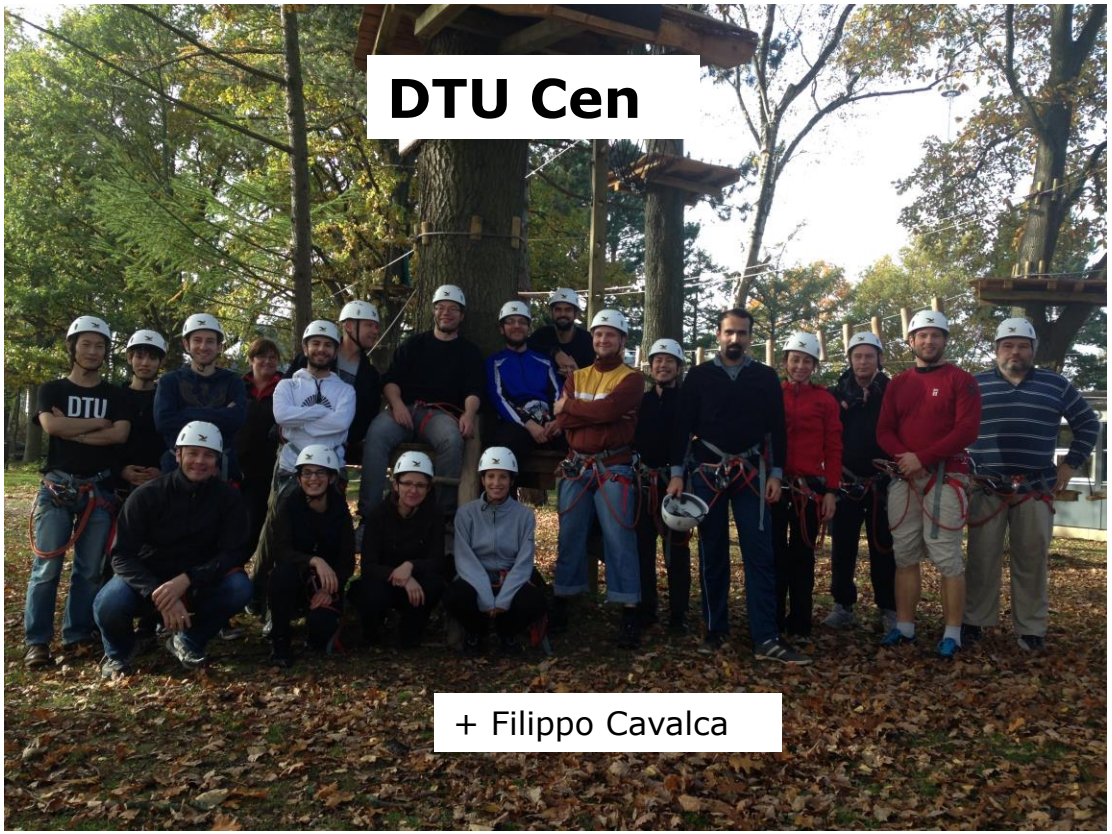

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