ThermoFisher SCIENTIFIC

In situ observation of chemical reaction inside a micro reaction capsule in SEM/DualBeam

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Application and Product Specialist EMEA

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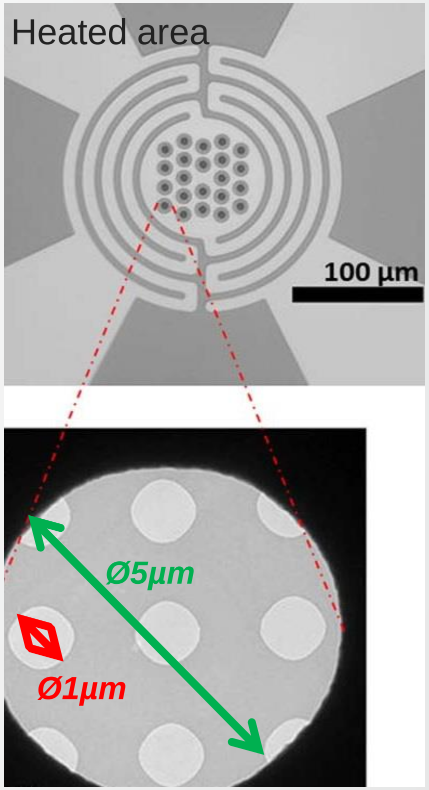
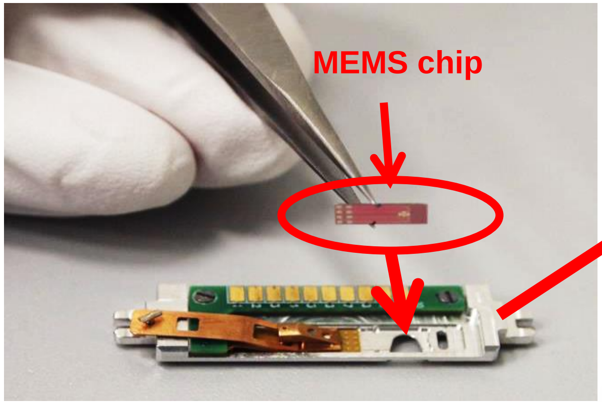
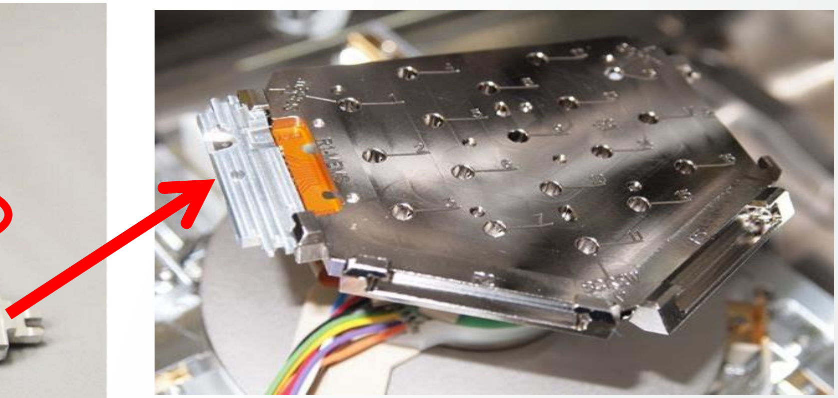
µHeater – MEMS based heating device

- Microheating device based on MEMS technology-solution for TEM & SEM/DualBeam, under high vacuum
- Compatible with all types of detectors: SE, BSE, STEM, EDS, EBSD
- Temperature up to 1200°C
- Maximum ramping speed: up to 10^4 °C/s
  - Software allows any slower rate
- No compromise in the SEM resolution
- No stage limits (incl. full rotation)
- Support sample size: nm ~ hundred µm



Ref: DOI: 10.1002/jemt.22623



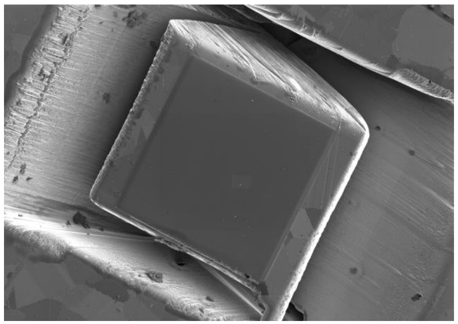
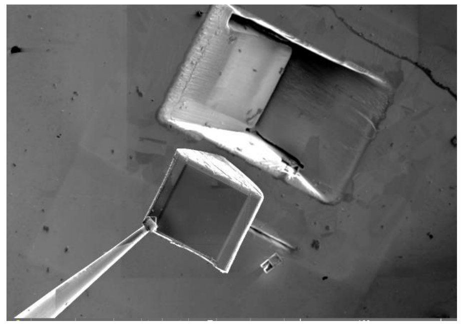
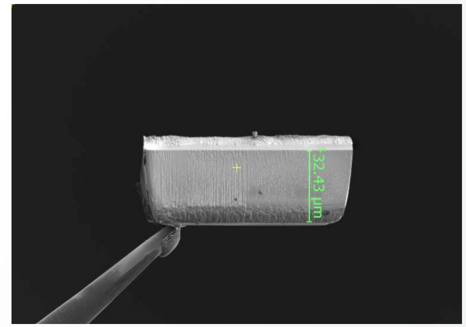


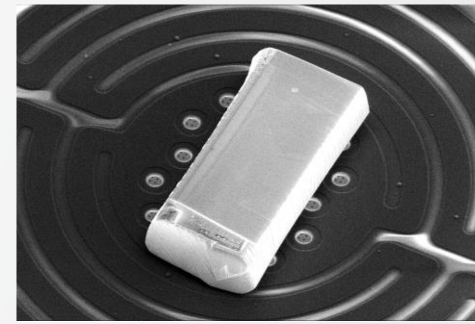
Multipurpose holder with slot for µHeater cartidge

µHeater sample preparation

A: Chunk fabrication using FIB

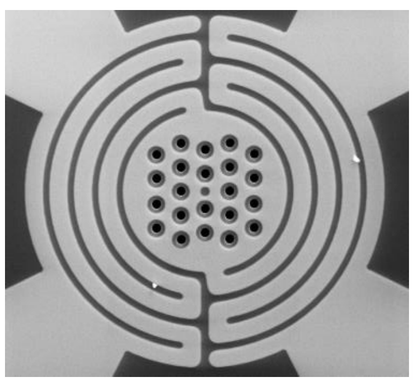
1. Chunk fabricated from bulk **2. FIB lift out** **3. On-needle cleaning** **4. Chunk on MEMS heater**

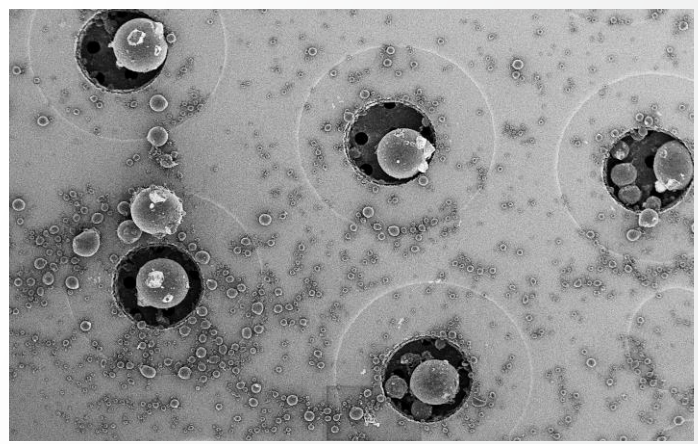


80µm x 35µm Ni superalloy chunk on MEMS chip.

B: Nanoparticles, powders

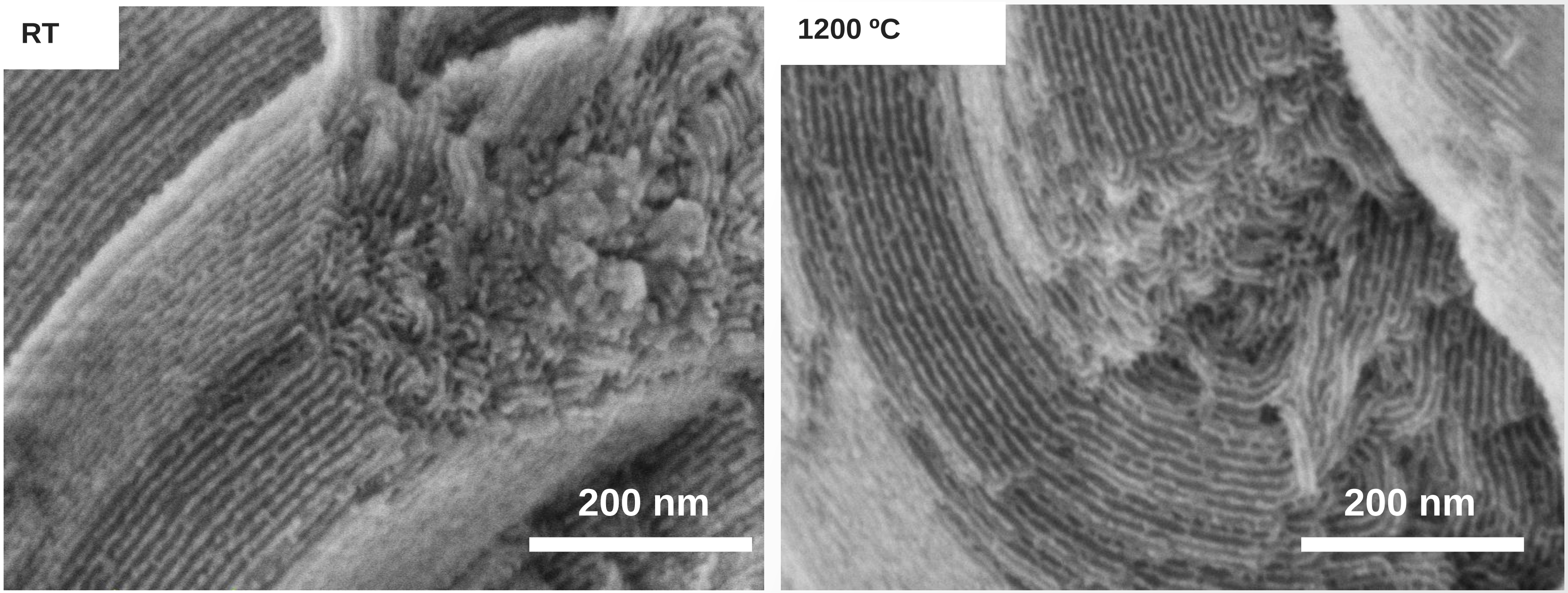



Mesoporous silica SBA-15



Sn nanoparticles on MEMS chip. The HFW is 41.2µm.

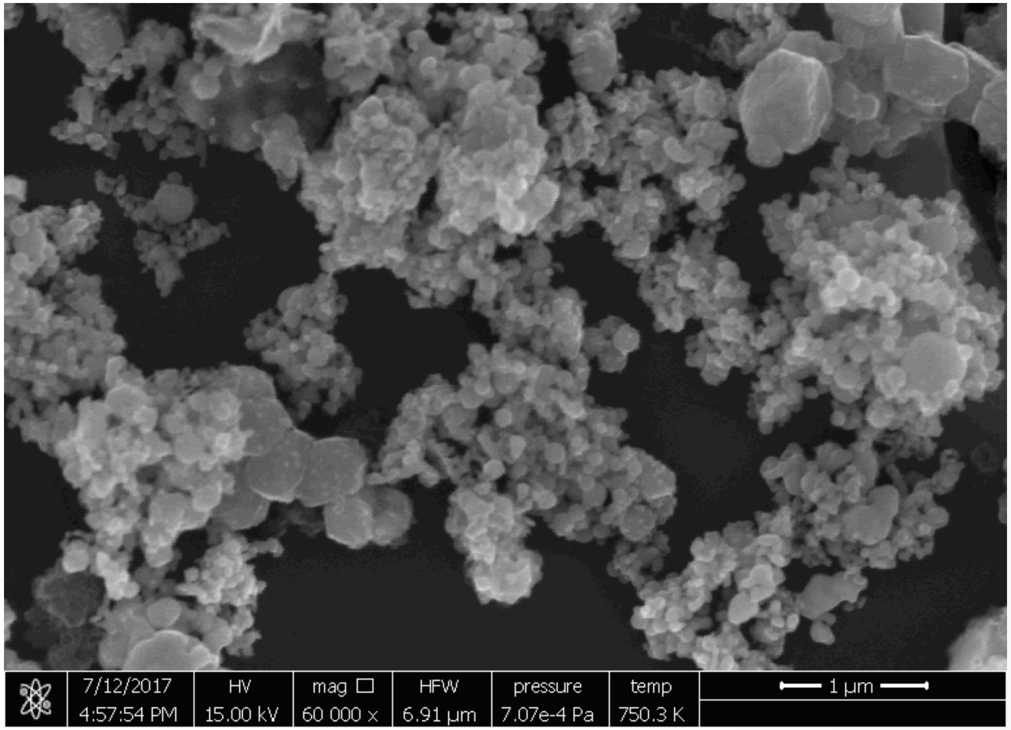
High resolution during heating on µHeater



The HFW is 690 nm.

SBA15 nanoparticles on µHeater. The nanoparticles were heated from room temperature to 1200ºC at a heating rate of 1000ºC/s. SE image was taken at room temperature and at 1200ºC. It shows high resolution images can be taken even at 1200ºC on µHeater.

µHeater – 1200° C heating with millisecond temperature control



Mix of Sn, Cu, Ag nanoparticles heated from 477° to 1200° C in real time
Image courtesy: Min Wu, Thermo Fisher Brno

µHeater: Extreme ramp rate, stability and image quality

µHeater:

- Ramp up to 1200° C in 100 ms
- 100 µm sample size

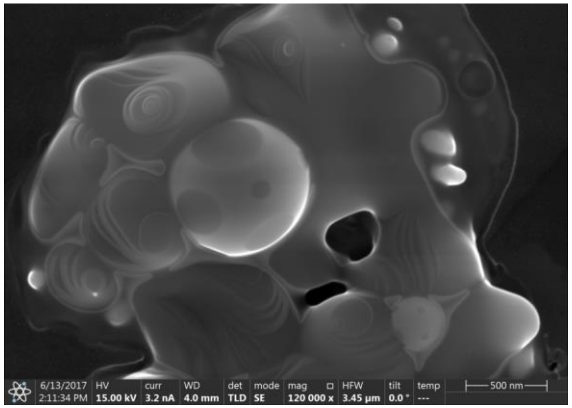
Benefits:

- Observation of rapid heating effects
- Work at high magnification

➢ Enables practical nanoparticle heating experiments

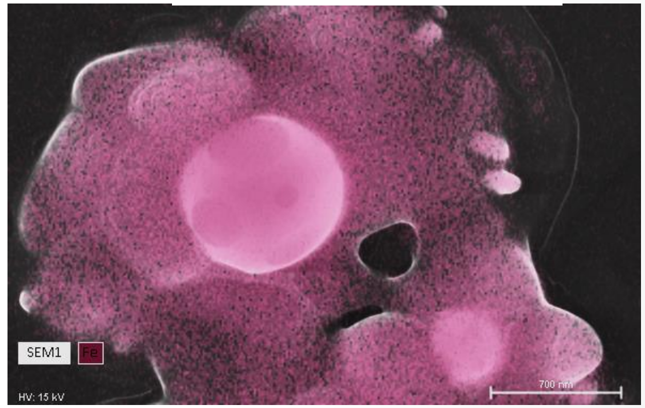
µHeater enables in situ EDS at Elevated Temperature

1050° C

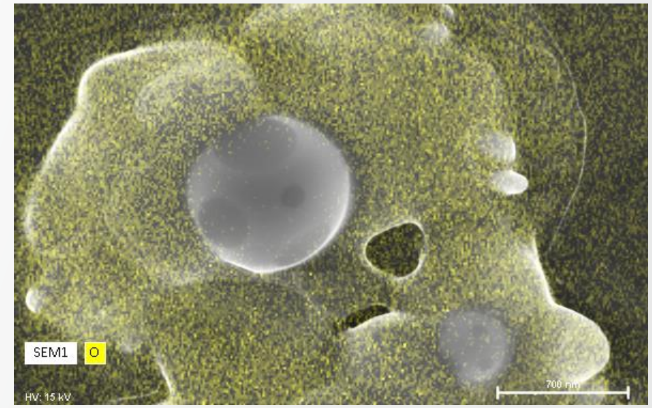


SE

Image courtesy: Min Wu, Thermo Fisher Brno



Iron (Fe)

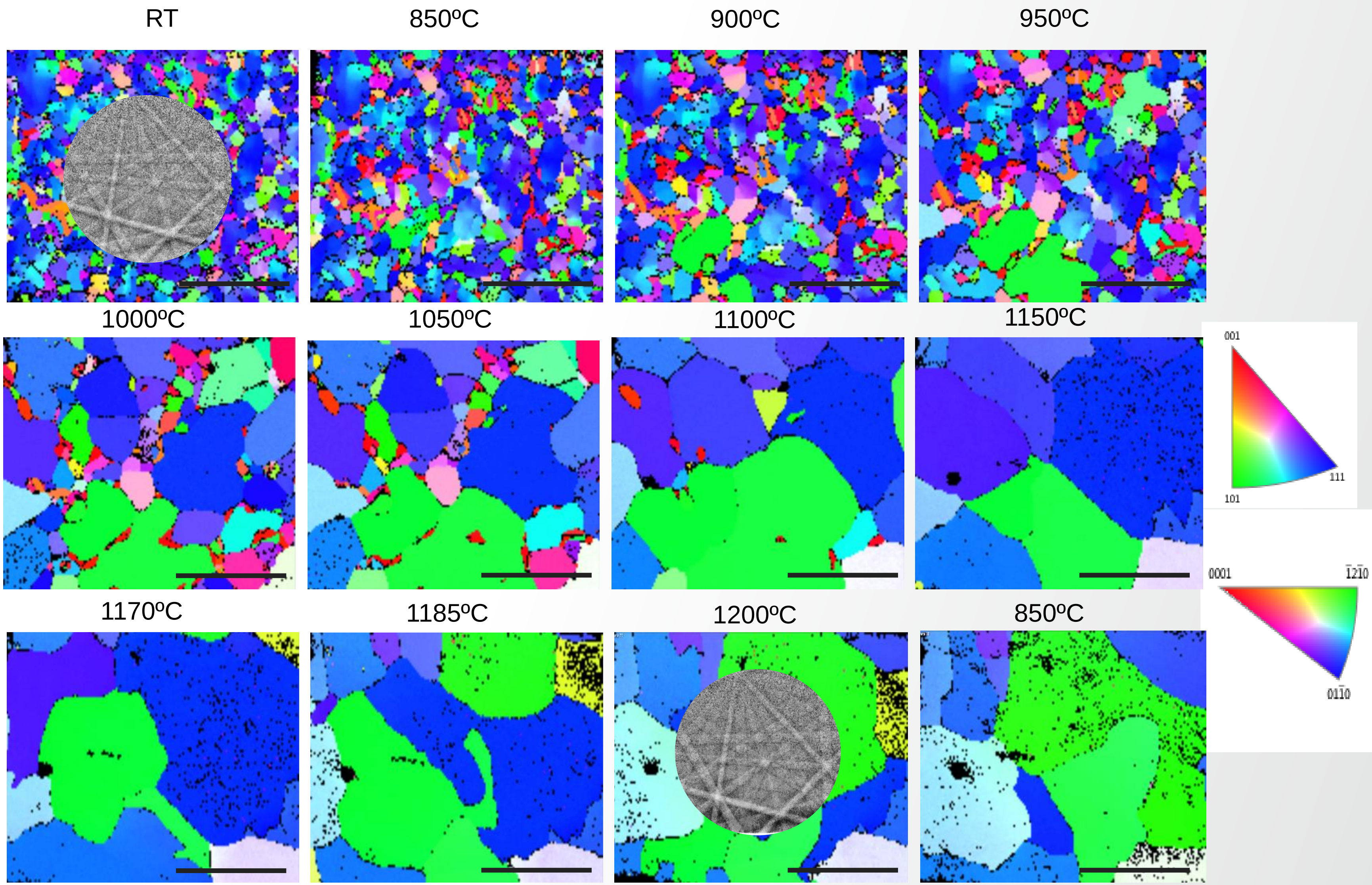


Oxygen (O)

- Magnetite-hematite shows elemental separation during melting
- Small footprint: no effects on imaging and detection
- EDS signal remains reliable even at high temperature

µHeater: high quality, high temperature analytics

µHeater enables in situ EBSD at Elevated Temperature

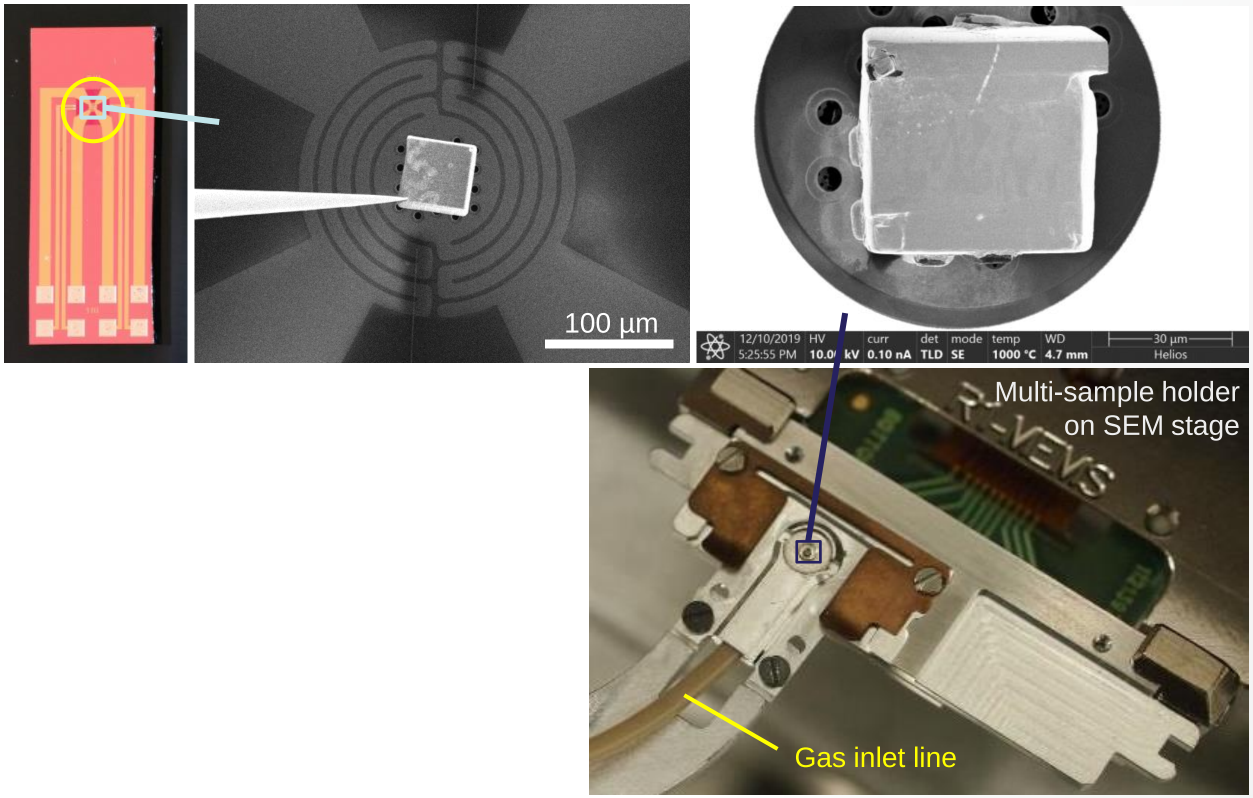


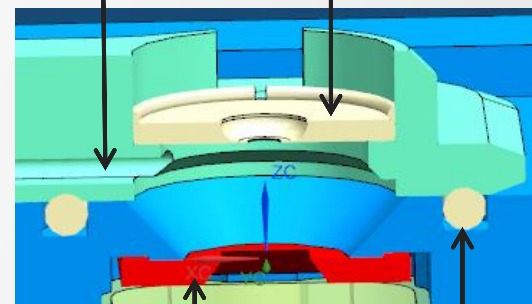
Sequential original IPFZ maps show a distinct recrystallization and grain growth (grain boundary migration) process at elevated temperatures. Each map was acquired at 20kV, 11nA, with a step size 0.3µm, in approximately 7 minutes. Scale bar in each map is 20µm.

Image courtesy: Min Wu, Thermo Fisher Brno

Ti-6Al-4V alloy

µReactor enable real time chemical reaction





Reactor volume: 7 µl
Inlet flow rate: units of sccm
Max. pressure: 500 Pa
(<1E-2 Pa in SEM chamber)

Titanium oxidation growth

Ti substrate

Temperature 850ºC

Acetone vapor (~ 100 Pa)

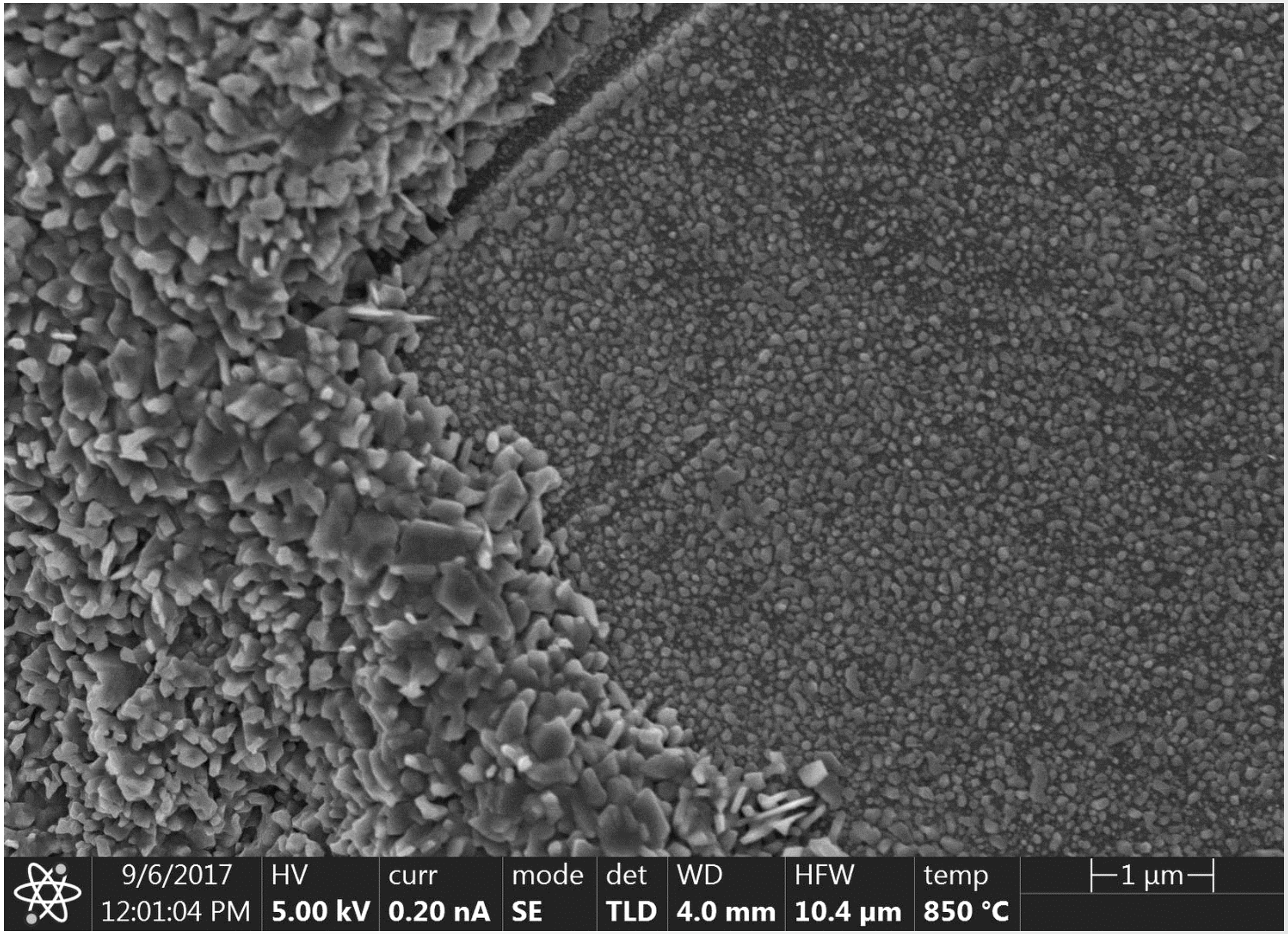
Formation of TiO_2 crystals

Imaging:

UHR mode of Helios

TLD-SE in-column detection

Acquisition as it is
(no registrations
no drift correction)

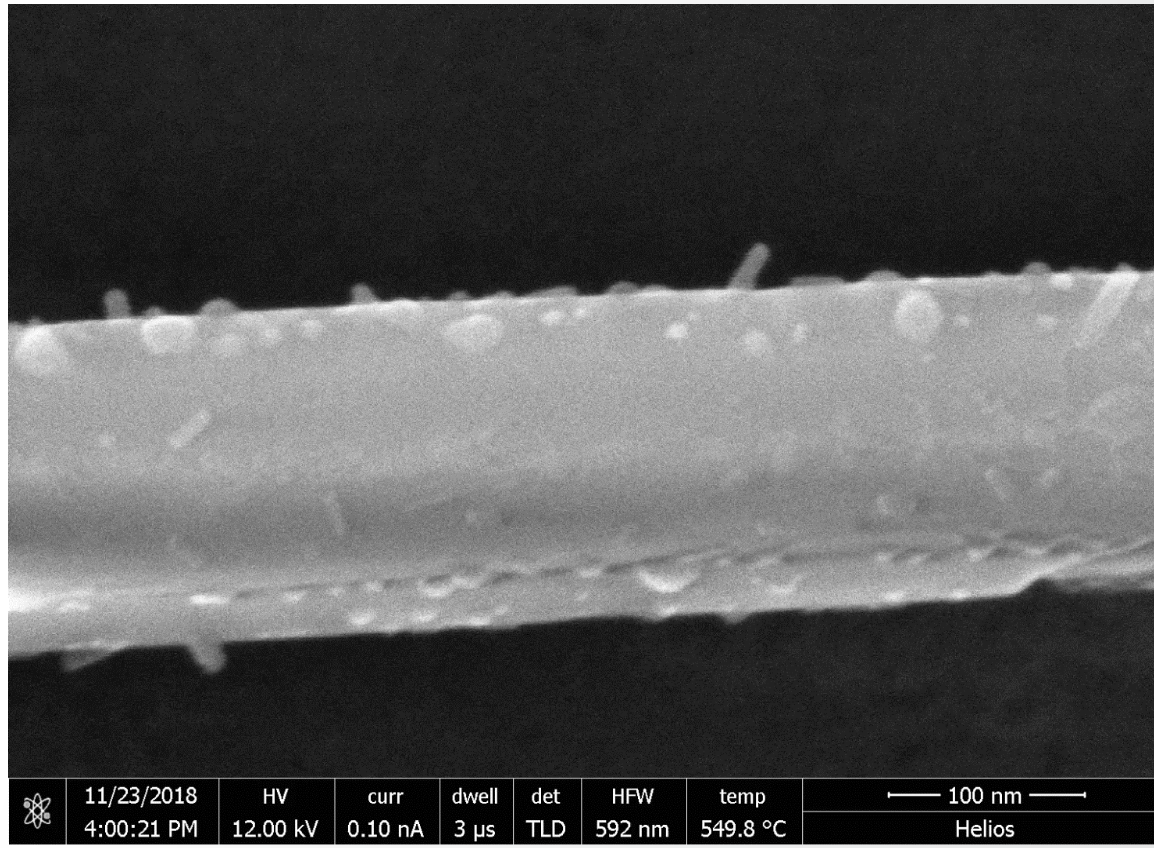


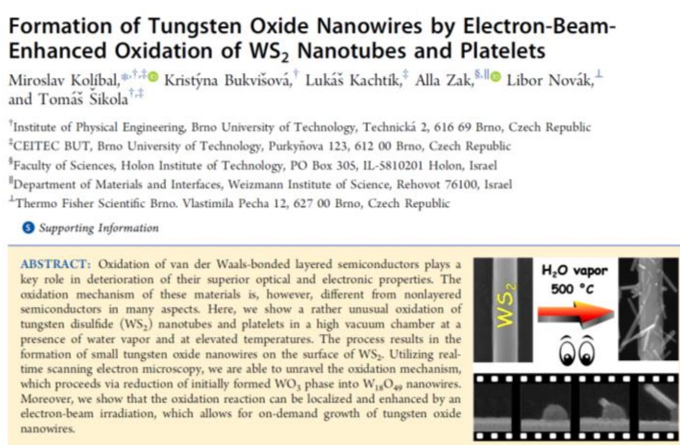
Tungsten oxide nanowires from WS_2

WS_2 sample oxidized in water vapor, forming tungsten oxide nanowires.

t = 700°C, p(H_2O) ~ 50 Pa

High resolution imaging in UHR mode in gas.





Formation of Tungsten Oxide Nanowires by Electron-Beam-Enhanced Oxidation of WS_2 Nanotubes and Platelets

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Supporting Information

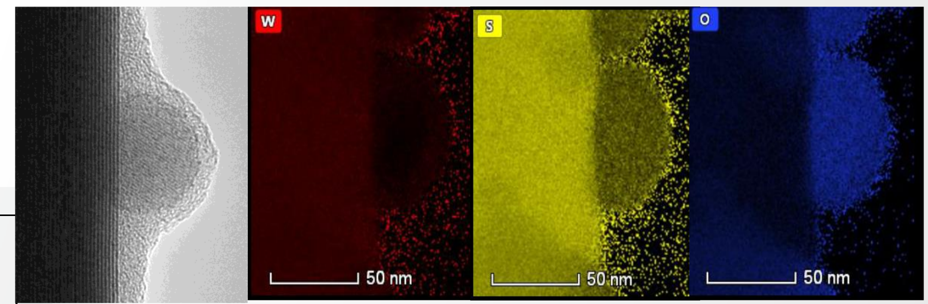
ABSTRACT: Oxidation of van der Waals-bonded layered semiconductors plays a key role in deterioration of their superior optical and electronic properties. The oxidation mechanism of these materials is, however, different from nonlayered semiconductors in many aspects. Here, we show a rather unusual oxidation of tungsten disulfide (WS_2) nanotubes and platelets in a high vacuum chamber at a presence of water vapor and at elevated temperatures. The process results in the formation of small tungsten oxide nanowires on the surface of WS_2. Utilizing real-time scanning electron microscopy, we are able to unravel the oxidation mechanism, which proceeds via reduction of initially formed WO_3 phase into $W_{18}O_{49}$ nanowires. Moreover, we show that the oxidation reaction can be localized and enhanced by an electron-beam irradiation, which allows for on-demand growth of tungsten oxide nanowires.

DOI: 10.1021/acs.jpcc.9b00592

Tungsten oxide nanowires from WS_2

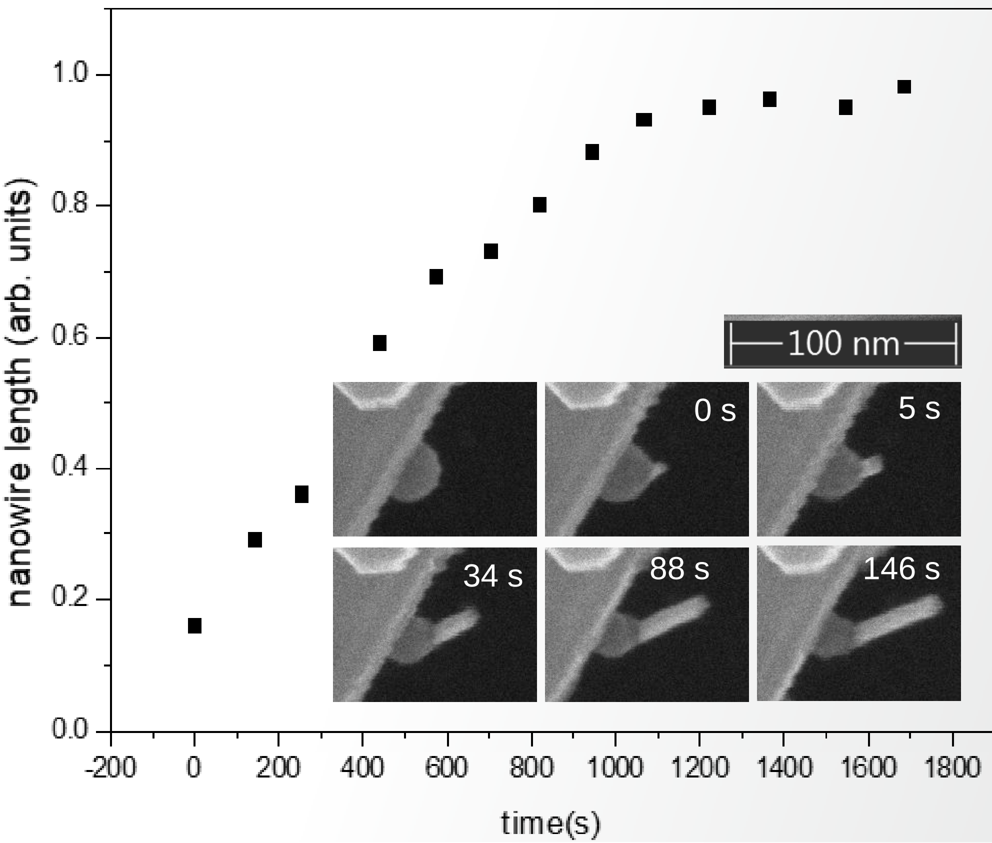
MEMS chip compatible with TEM (NanoEx)

Start: sulfur oxide droplet

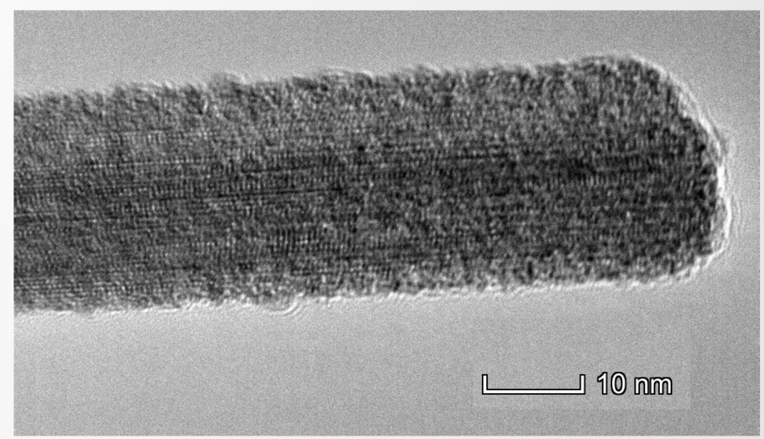


W:	17.0 %
S:	0.0 %
O:	82.6 %

Growth kinetics from UHR SEM images:



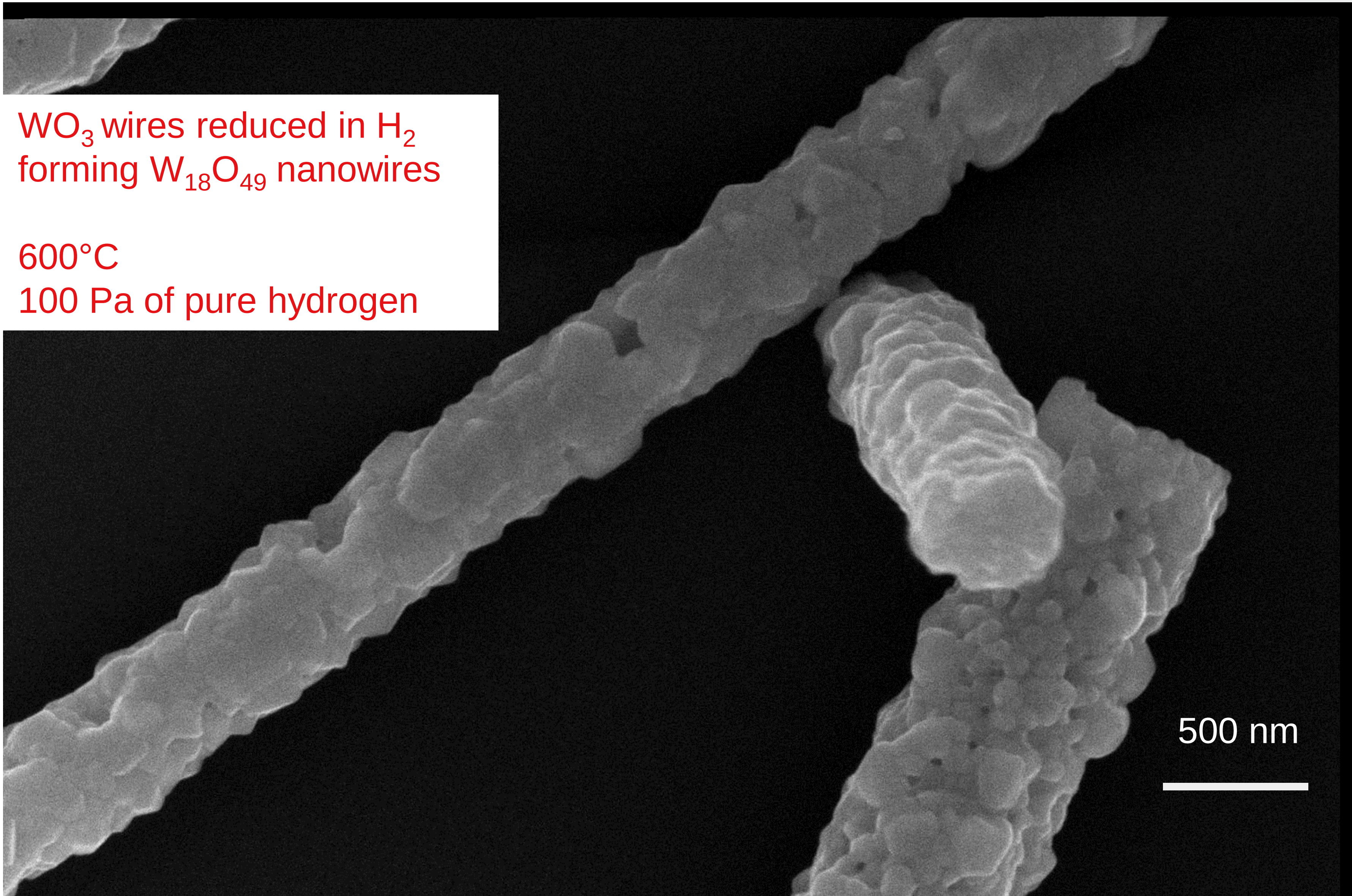
Tungsten oxide wire



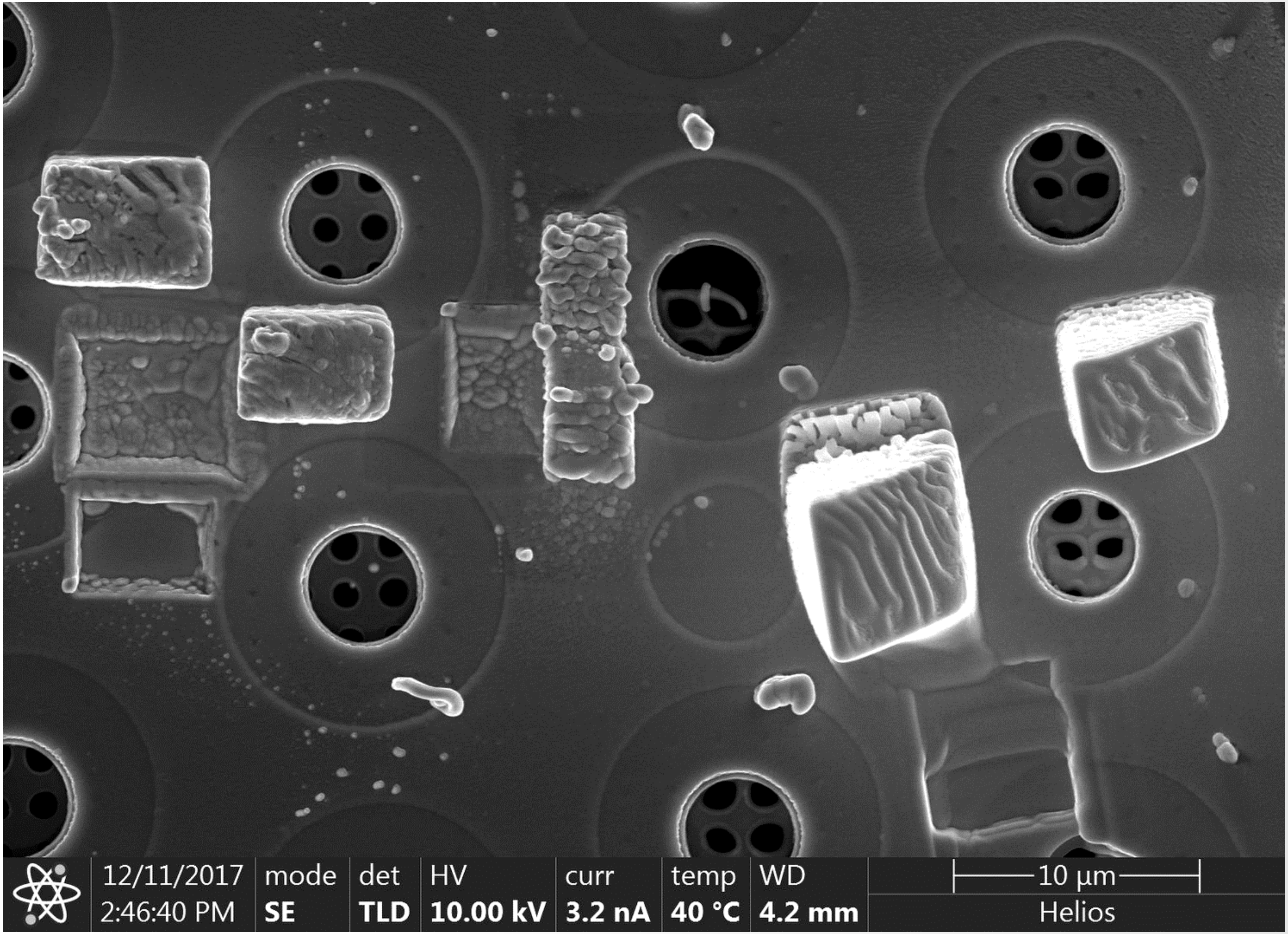
Tungsten oxide nanowires - reduction

WO_3 wires reduced in H_2
forming $W_{18}O_{49}$ nanowires

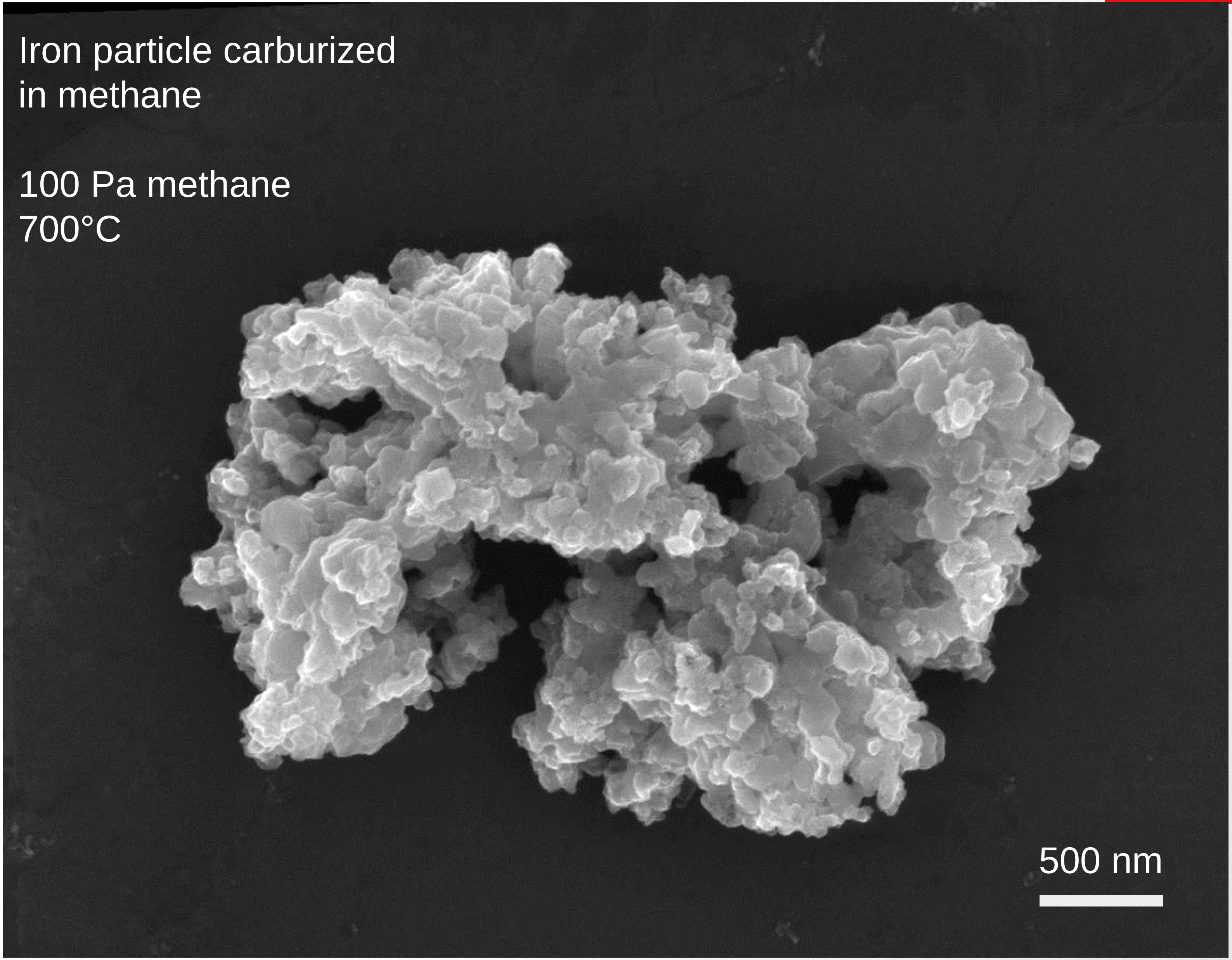
600°C
100 Pa of pure hydrogen



Pt-Ga wires growing in hydrogen

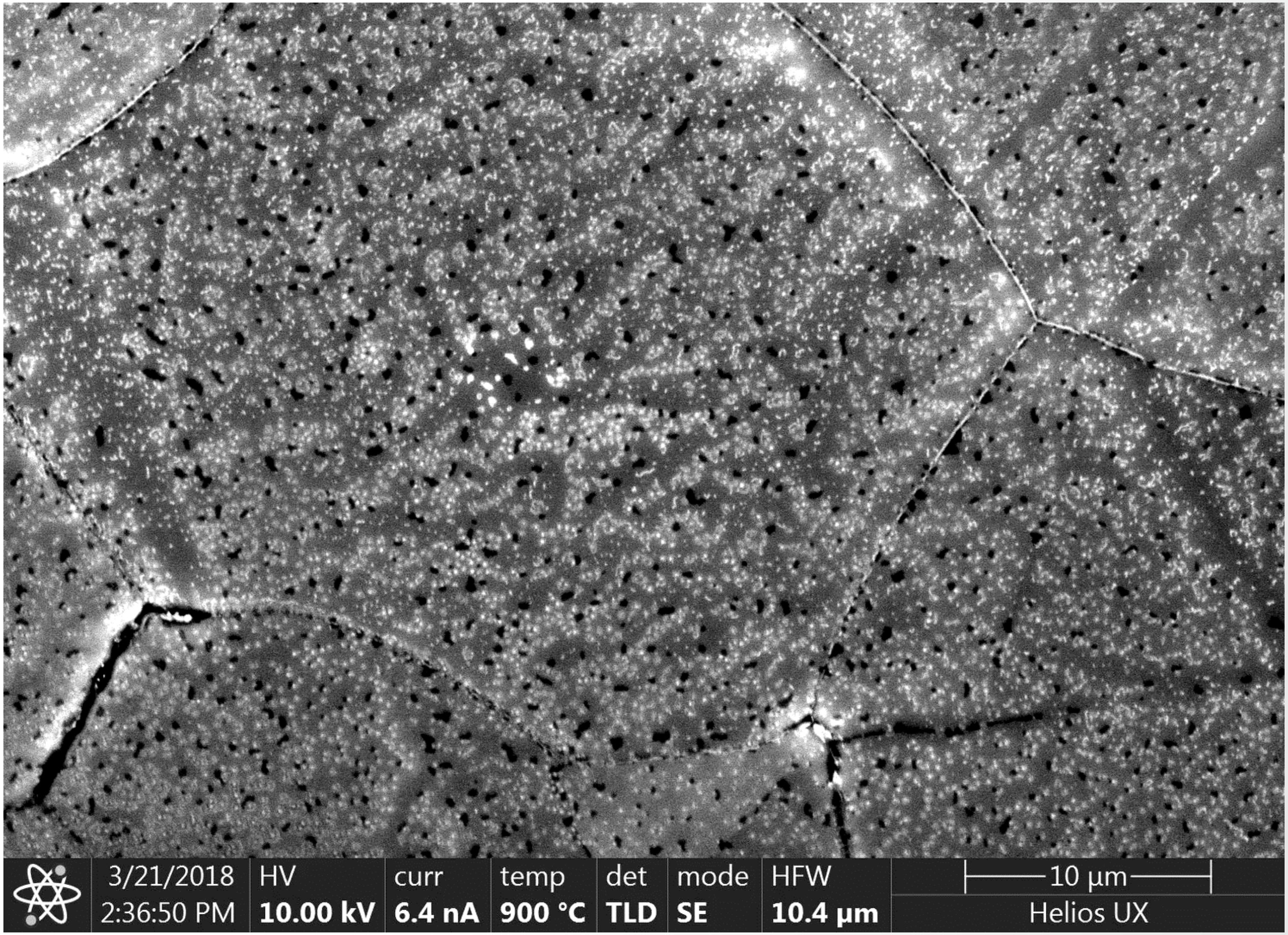


Iron carbide formation



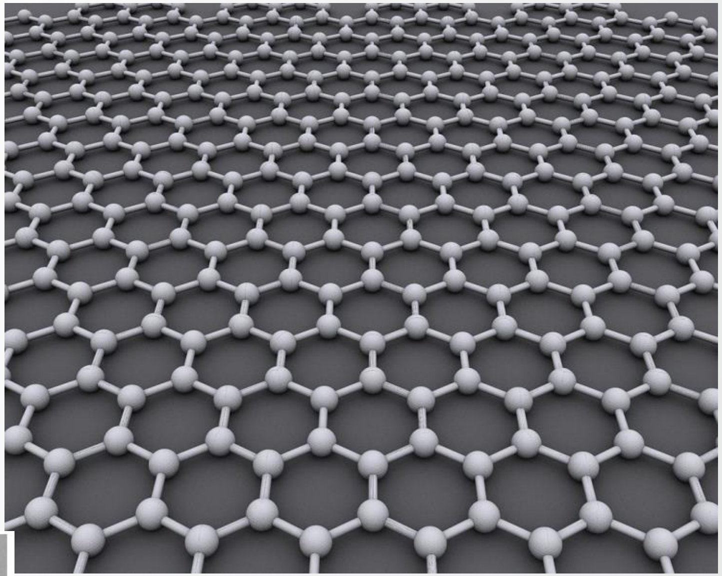
Copper cleaning in hydrogen

Polycrystalline copper (oxidized surface); Reduction in pure H_2 (50 Pa) at 1000ºC.

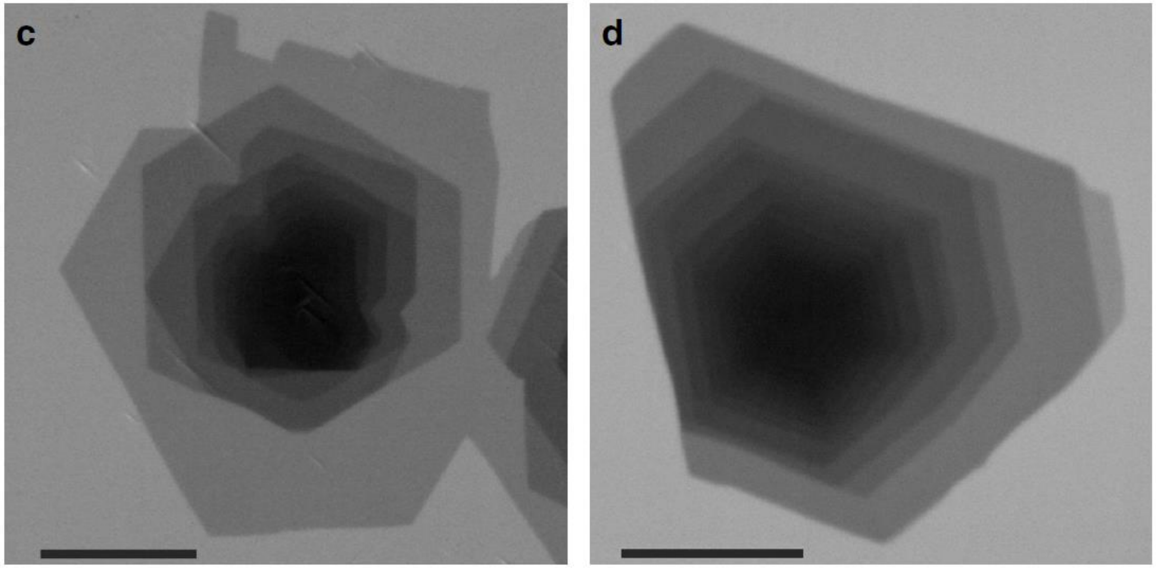


Chemical vapor deposition: graphene

One of production methods of graphene is the CVD, which can be maintained in the µReactor and *in situ* imaged by SEM.



Graphene layers visible in signal of secondary electrons



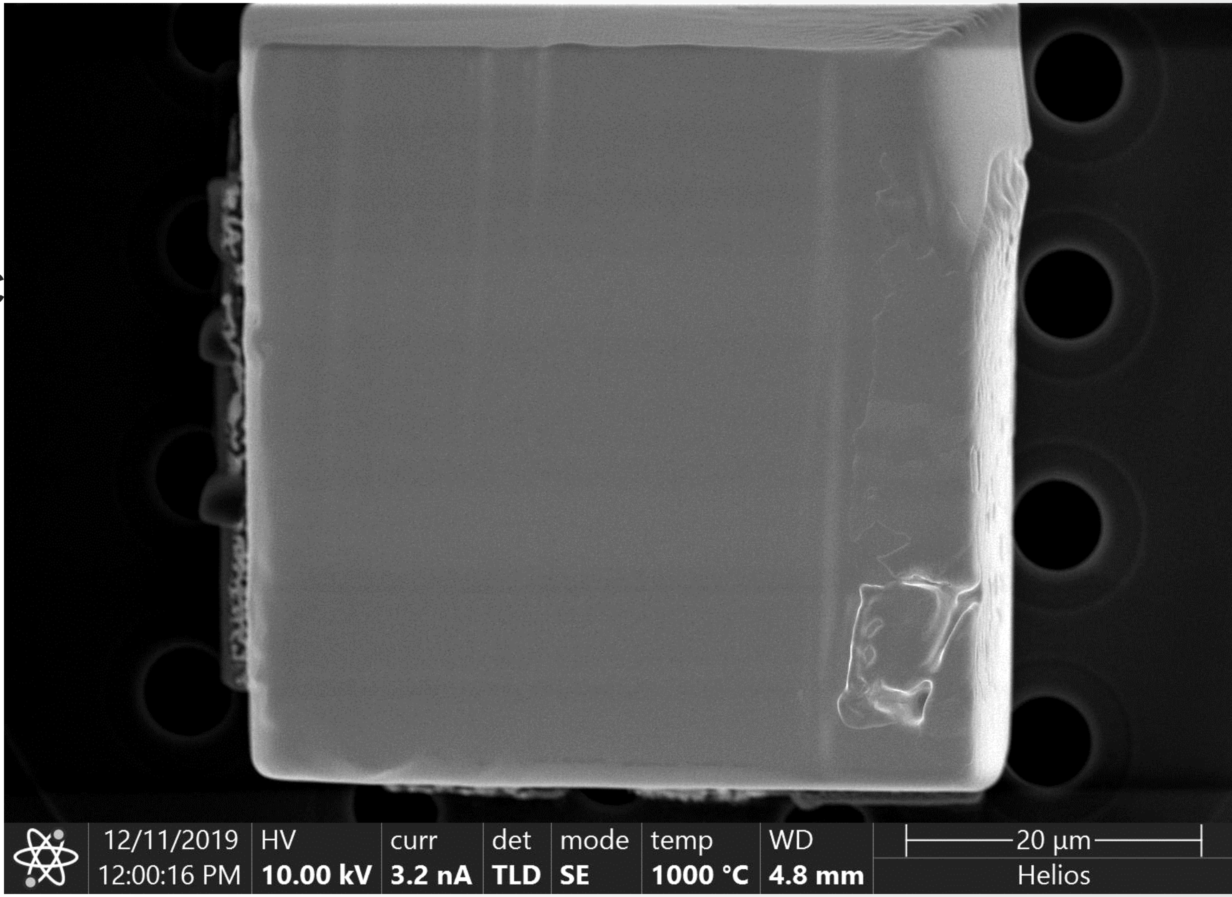
Growth Dynamics, Stacking Sequence and Interlayer Coupling in Few-Layer Graphene Revealed by in Situ SEM
Zhu-Jun Wang et al., 2017
Microscopy and Microanalysis 23(S1):1746-1747

Chemical vapor deposition: graphene

Pt sample was first cleaned in hydrogen at 1000°C (H_2 pressure 30 Pa).

Ethylene introduced at 1000°C (C_2H_4 pressure ~ 5 Pa) to grow graphene monolayer.

Graphene monolayer grows on polycrystalline Pt.

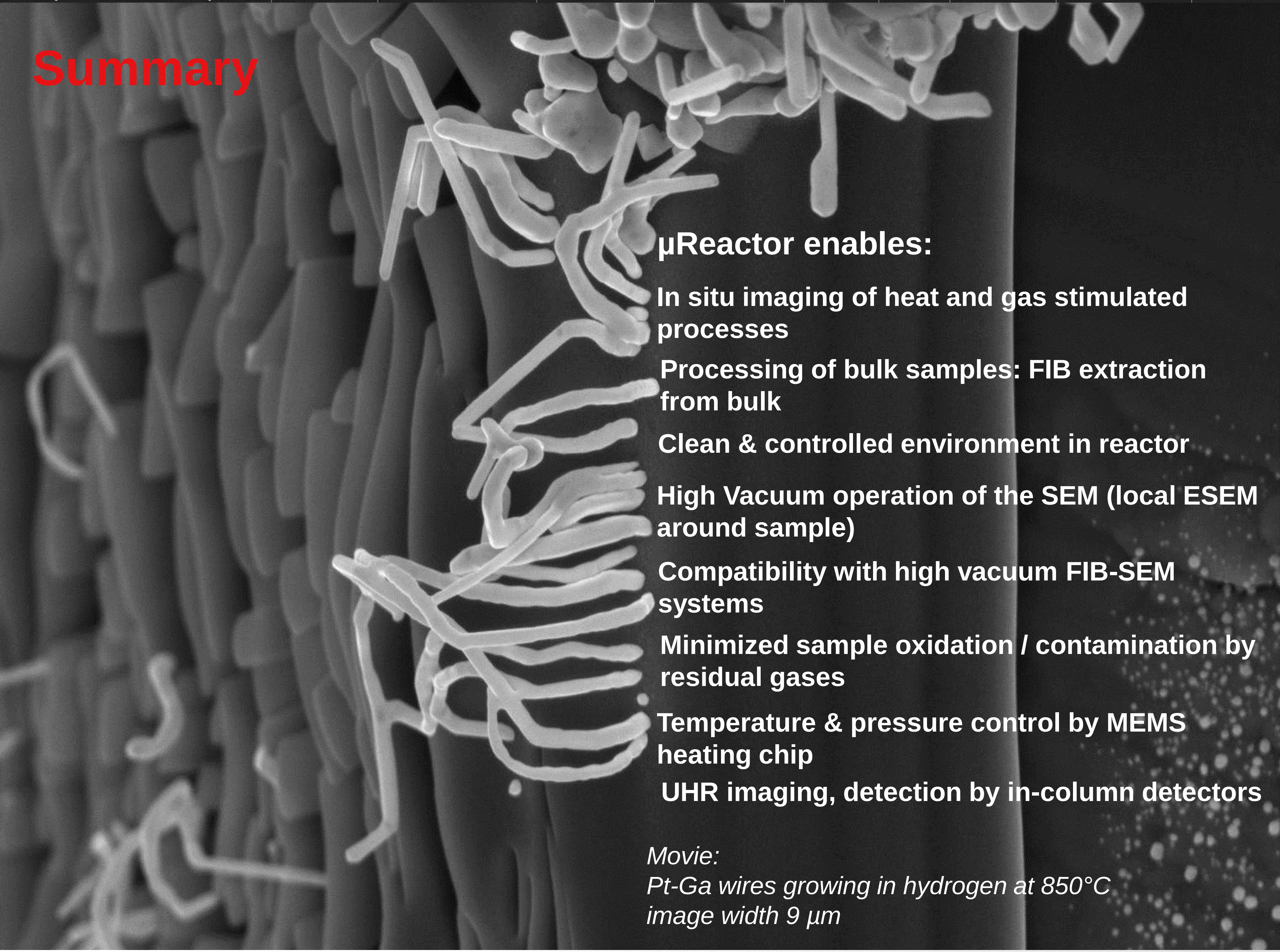


Publications with μReactor

M&M 2018
Control and in-situ imaging of heat & gas mediated processes in FIB/SEM system. (2018) Novak et al. *Microscopy and Microanalysis, 24*(S1), 808-9.

M&M 2020
Microreactor for Clean and Controlled In-situ SEM Imaging of CVD Processes (2020) Novak, L., Wandrol, P., & Vesseur, E. *Microscopy and Microanalysis, 26*(S2), 1144-5.

Collaboration with Ceitec & Brno University of Technology & Weizmann Institute
Formation of Tungsten Oxide Nanowires by Electron-Beam-Enhanced Oxidation of WS_2 Nanotubes and Platelets (2019) Kolibal et al, *Journal of Physical Chemistry C*, 123, 14, 9552–9



Summary

µReactor enables:

- **In situ imaging of heat and gas stimulated processes**
- **Processing of bulk samples: FIB extraction from bulk**
- **Clean & controlled environment in reactor**
- **High Vacuum operation of the SEM (local ESEM around sample)**
- **Compatibility with high vacuum FIB-SEM systems**
- **Minimized sample oxidation / contamination by residual gases**
- **Temperature & pressure control by MEMS heating chip**
- **UHR imaging, detection by in-column detectors**

Movie:
Pt-Ga wires growing in hydrogen at 850°C
image width 9 µm