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Innovative Materials For Additive Manufacturing
(IMAM)

Proceedings

3-12-2020

Additive manufacturing of multi-metals and multi-materials by electrohydrodynamic redox printing – towards 3D gradient materials with submicrometer resolution

Maxence Menétrey

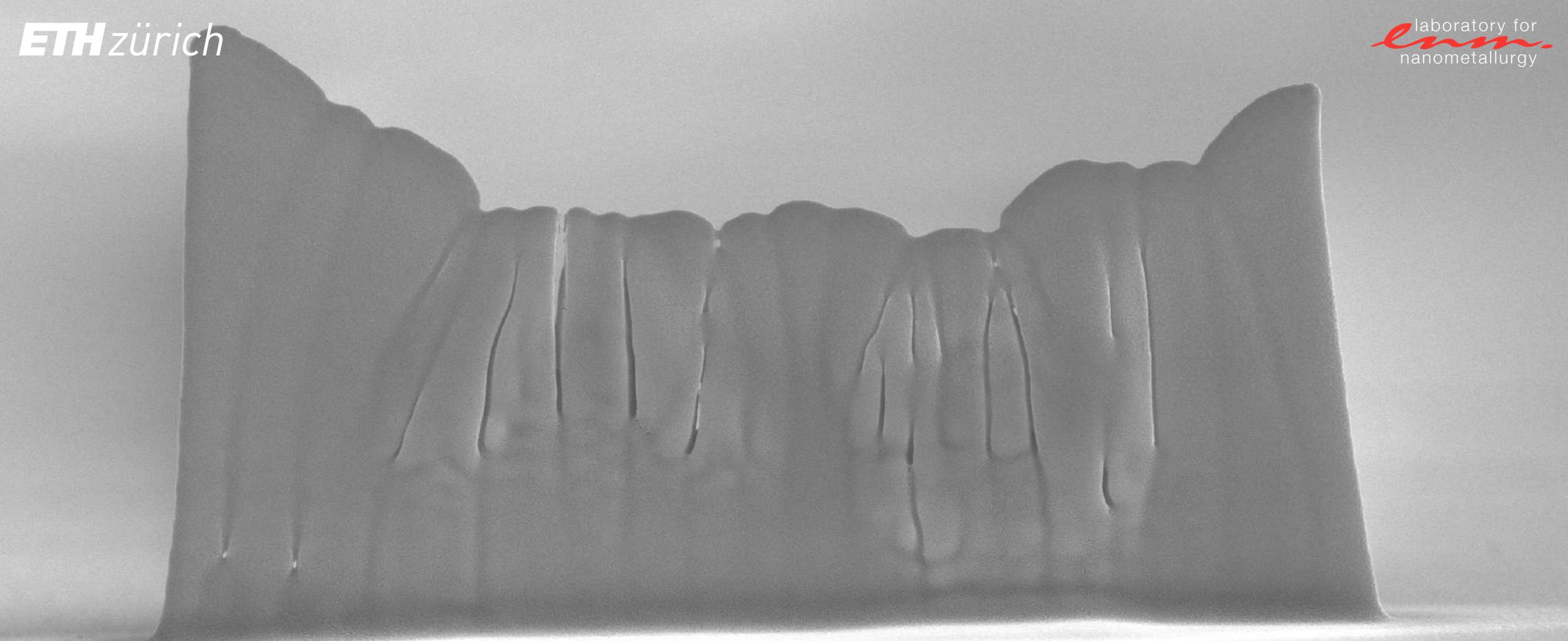
Alain Reiser

Lukas Koch

Mirco Nydegger

Ralph Spolenak

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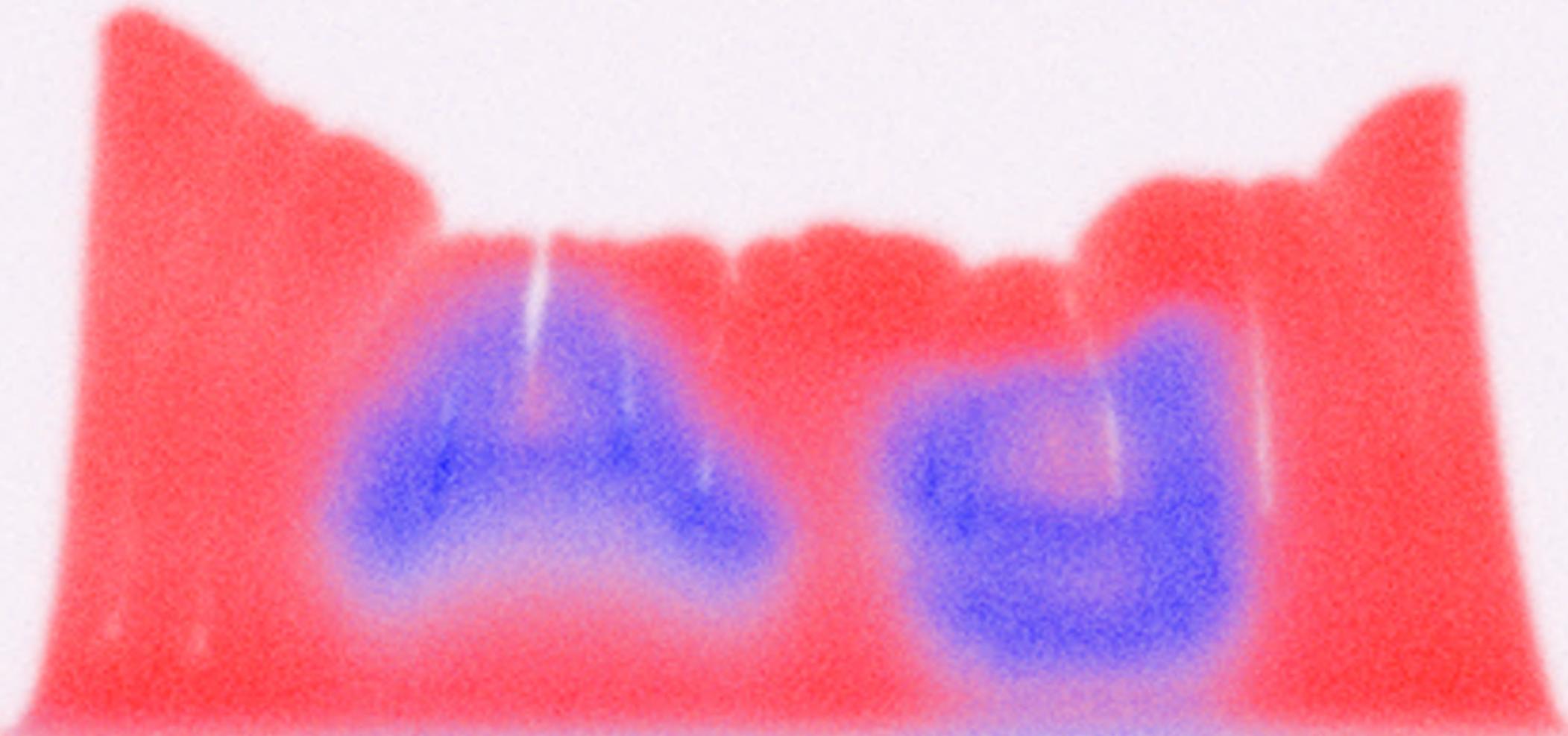


Additive manufacturing of metals at small length scales – microstructure, properties and novel multi-metal electrochemical concepts

Maxence Menétrey

1 μm





Additive manufacturing of metals at small length scales – microstructure, properties and novel multi-metal electrochemical concepts

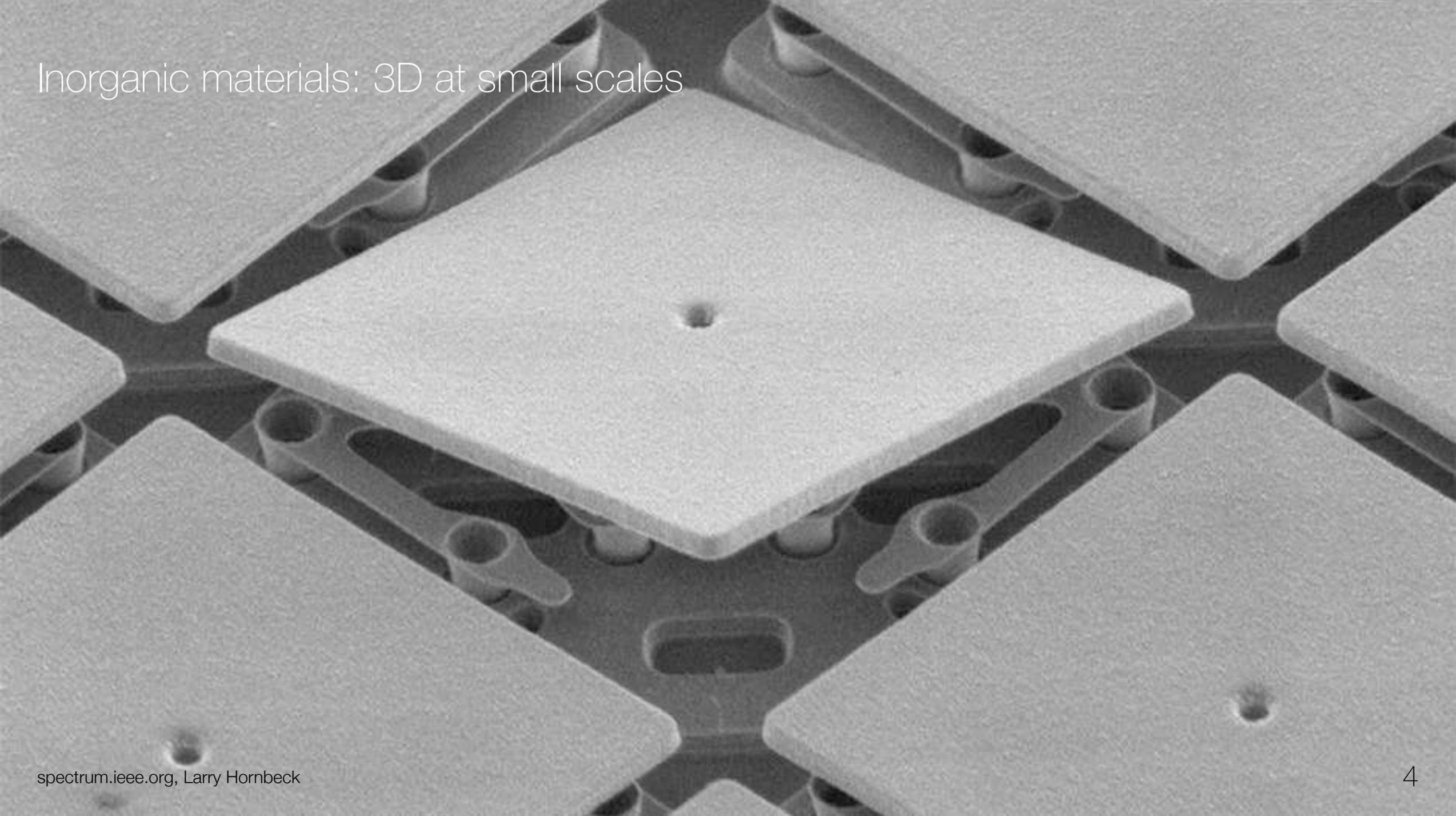
Maxence Menétrey

Maxence Menétrey, Alain Reiser, M. Lindén, L. Koch, M. Nydegger, A. Sologubenko, J. M. Wheeler, H. Galinski, R. Spolenak

A. Marchand, A. Pruska, P. Rohner, R. Zenobi, D. Poulikakos

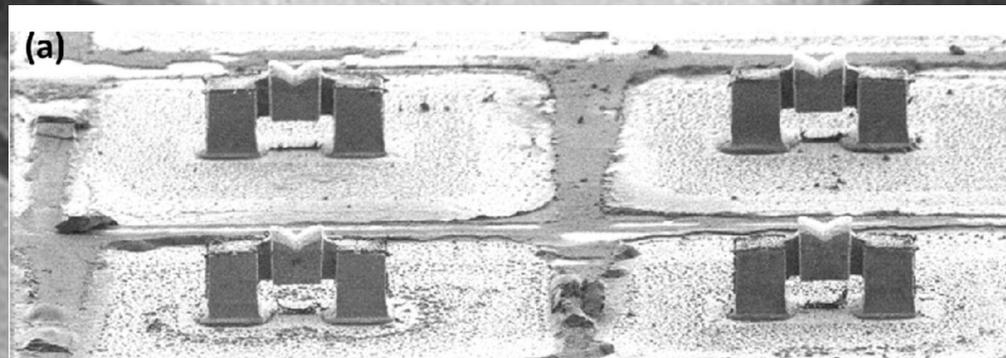
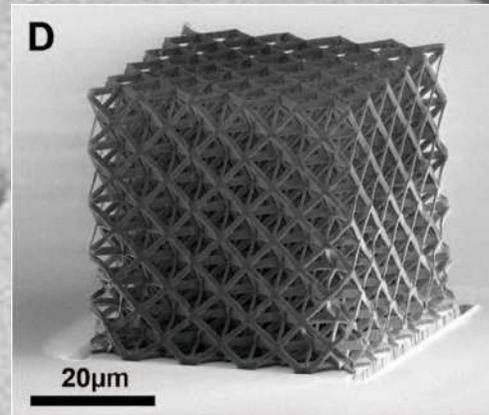
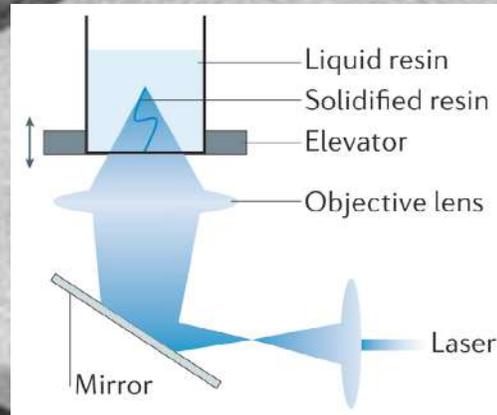
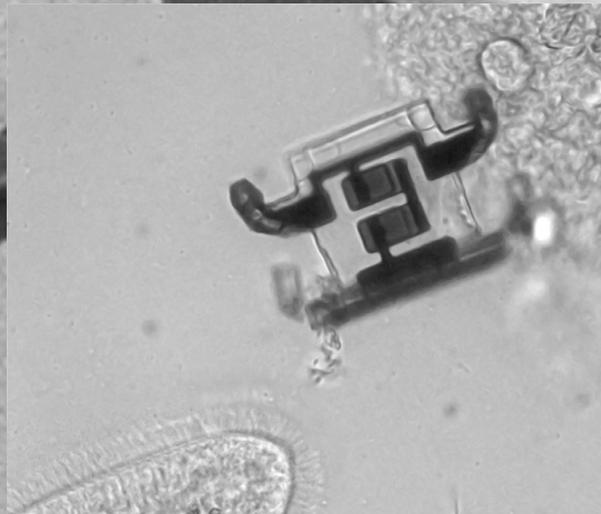
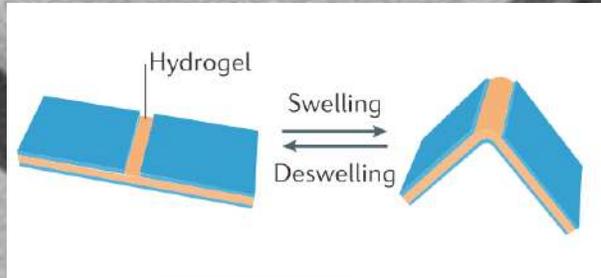
K. A. Dunn, T. Matsuura, F. Iwata, O. Fogel, Z. Kotler, Q. Shi, N. Zhou, J. Lewis, K. Charipar, A. Piqué, P. Rohner, D. Poulikakos, S. Lee, S. K. Seol, G. Bürki, I. Utke, C. van Nisselroy, T. Zambelli

Inorganic materials: 3D at small scales

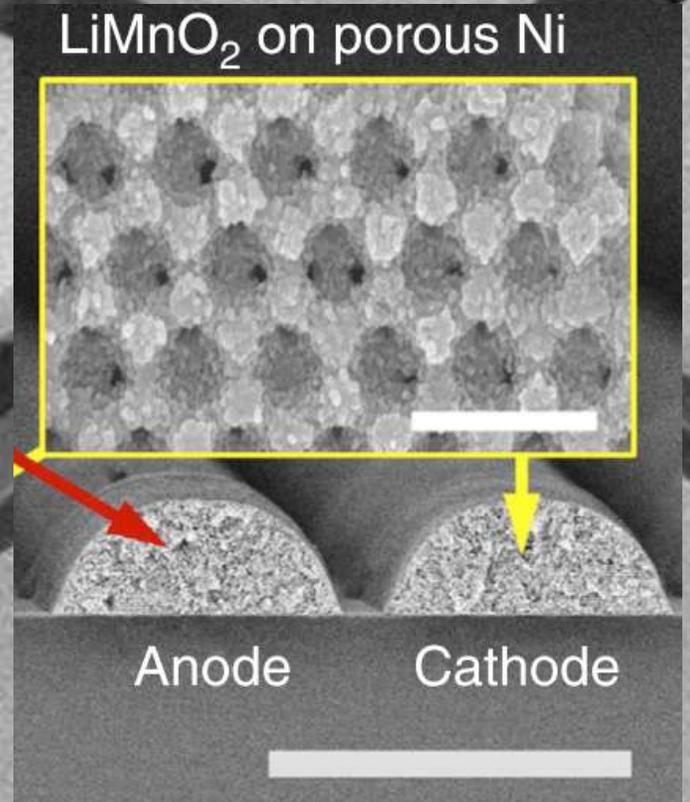


Inorganic materials: 3D at small scales

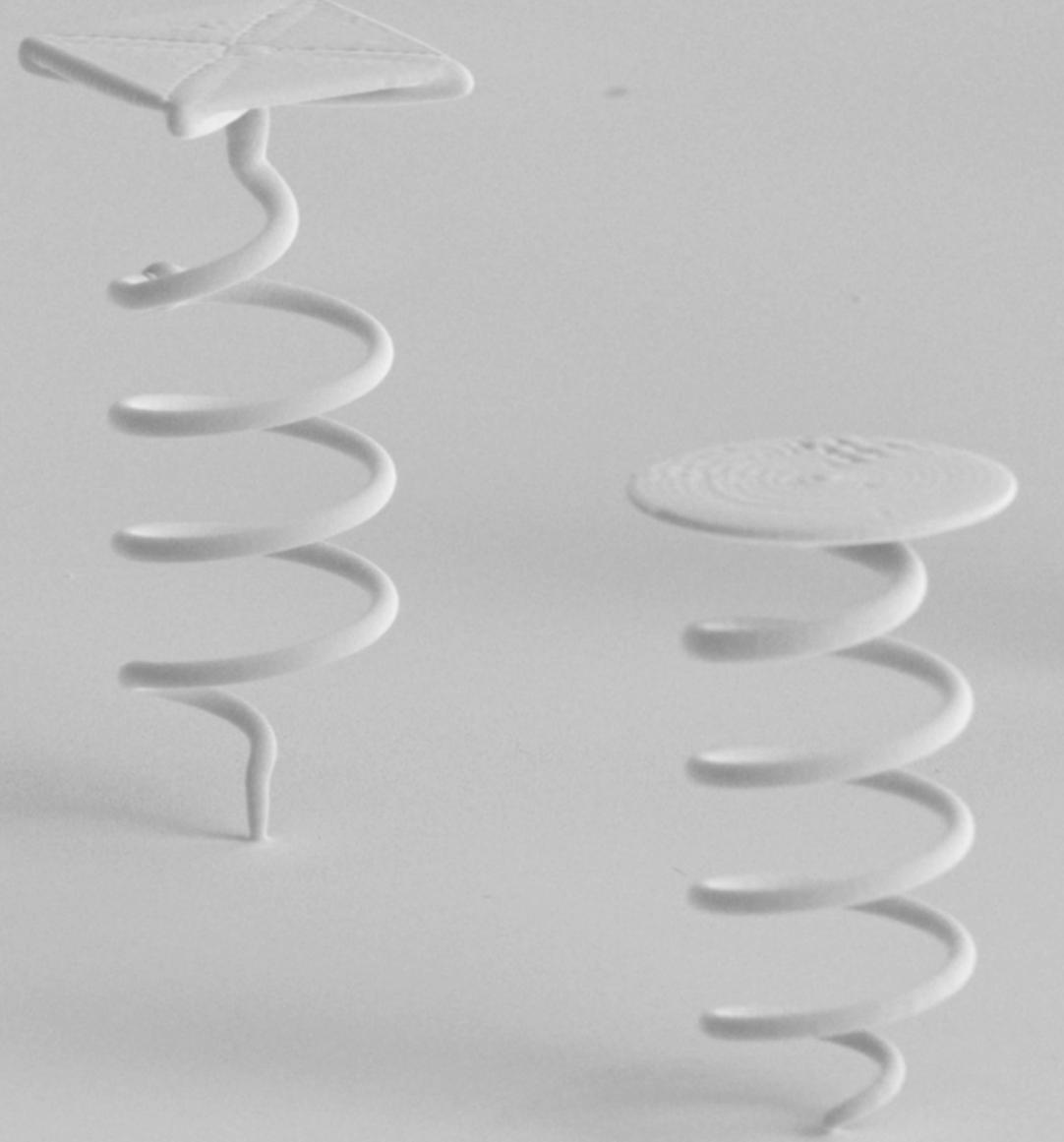
Buckling or folding



3D templating



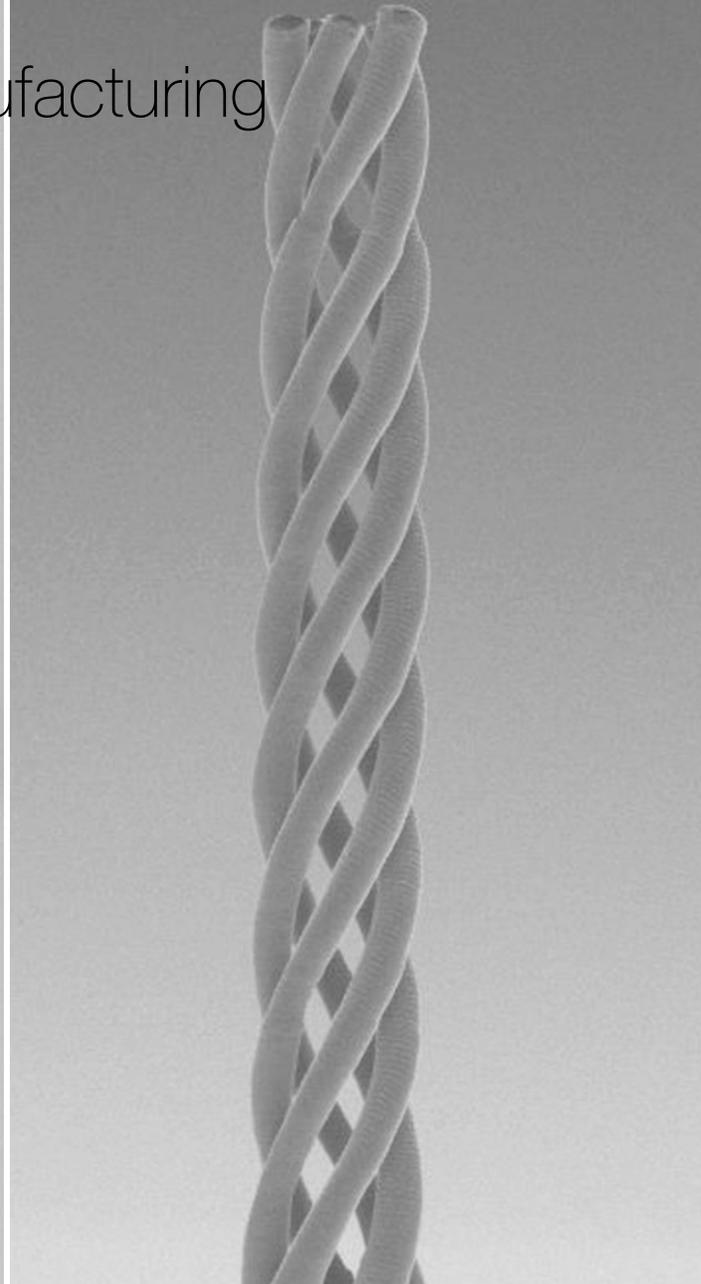
3D at small scales – additive manufacturing



Exaddon (former Cytosurge)
Hirt, L., et al., *Adv. Mater.* 28, 2311–2315 (2016).

20 μm

Lin, Y. et al., *Adv. Mater. Technol.* 4, 1800393 (2019).



5 μm

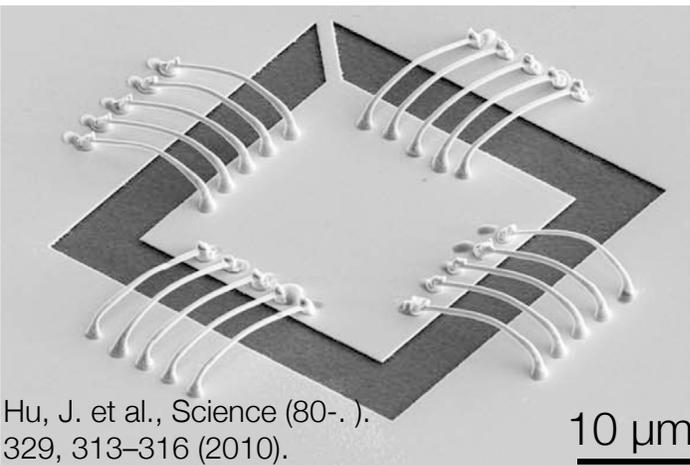
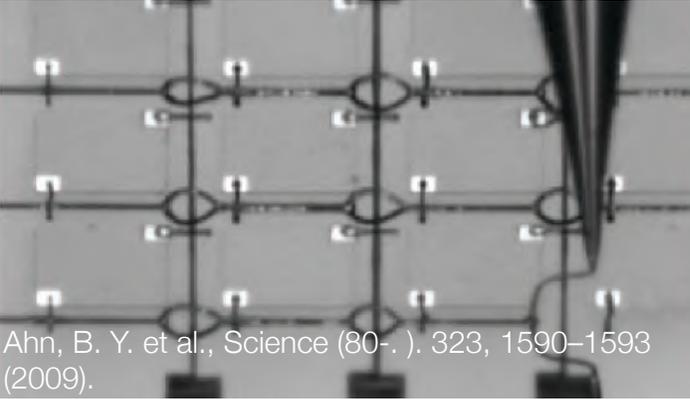


Exaddon (former Cytosurge)

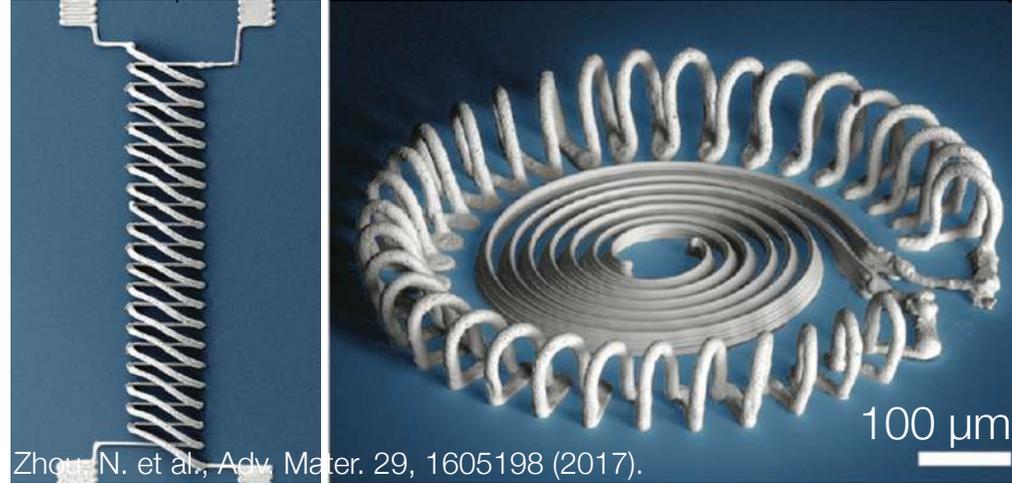
100 μm

Direct small-scale AM of metals: a future technology?

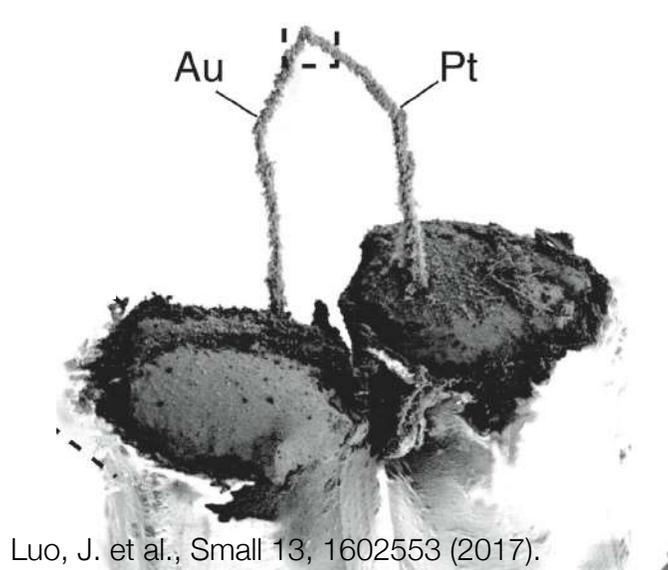
Electrical interconnects



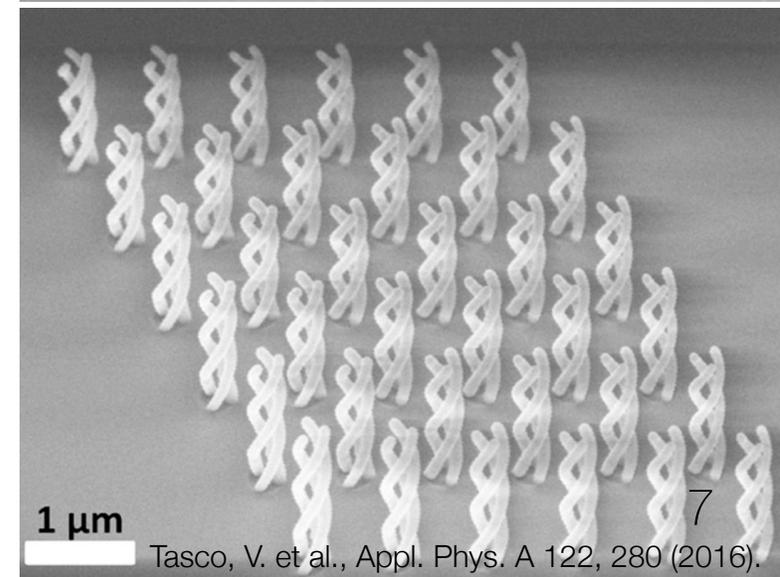
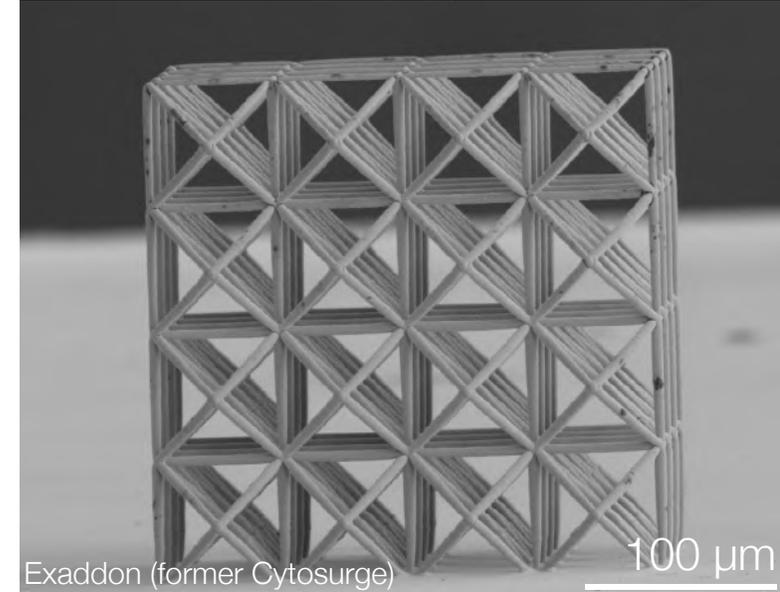
Out-of-plane circuit elements



Sensors



Lattice- and metamaterials



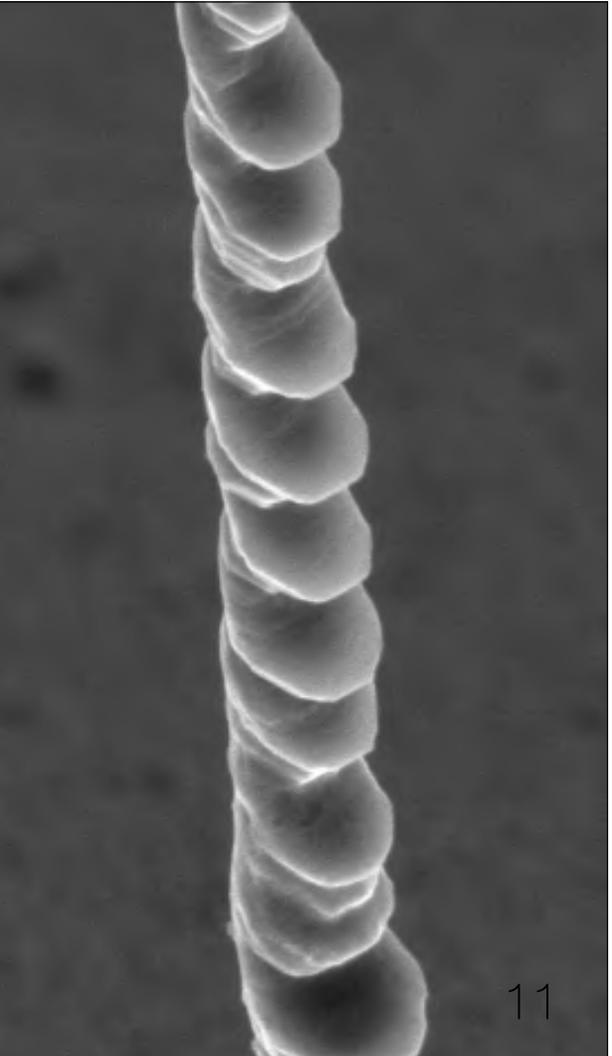
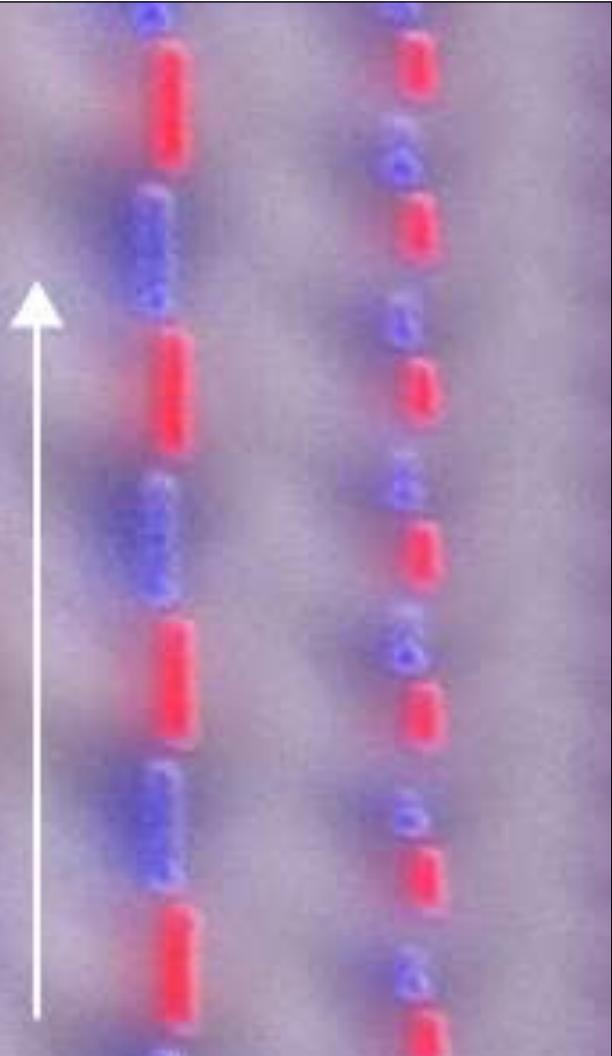
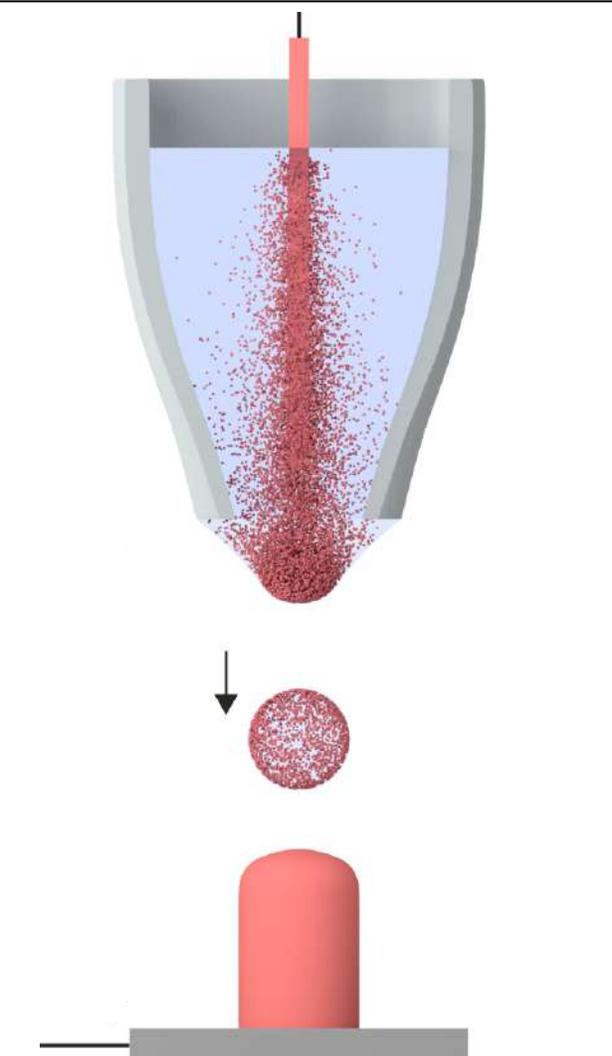
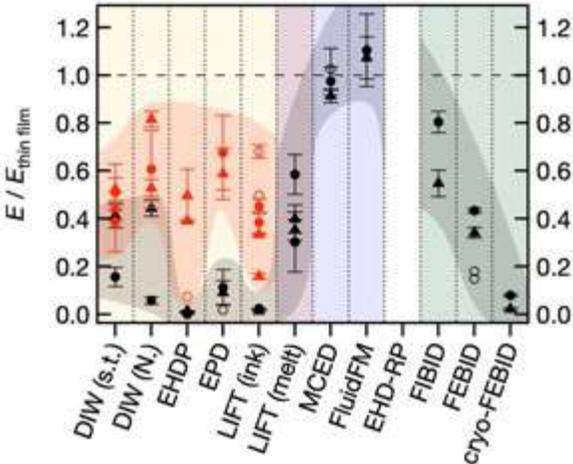
An overview of the talk

Part I: Microstructure and properties of printed metals

Part II: EHD-RP

Part III: Multi-metal EHD-RP

Part IV: Where to?



Part I: A study of the microstructure and mechanical properties of additively deposited metals

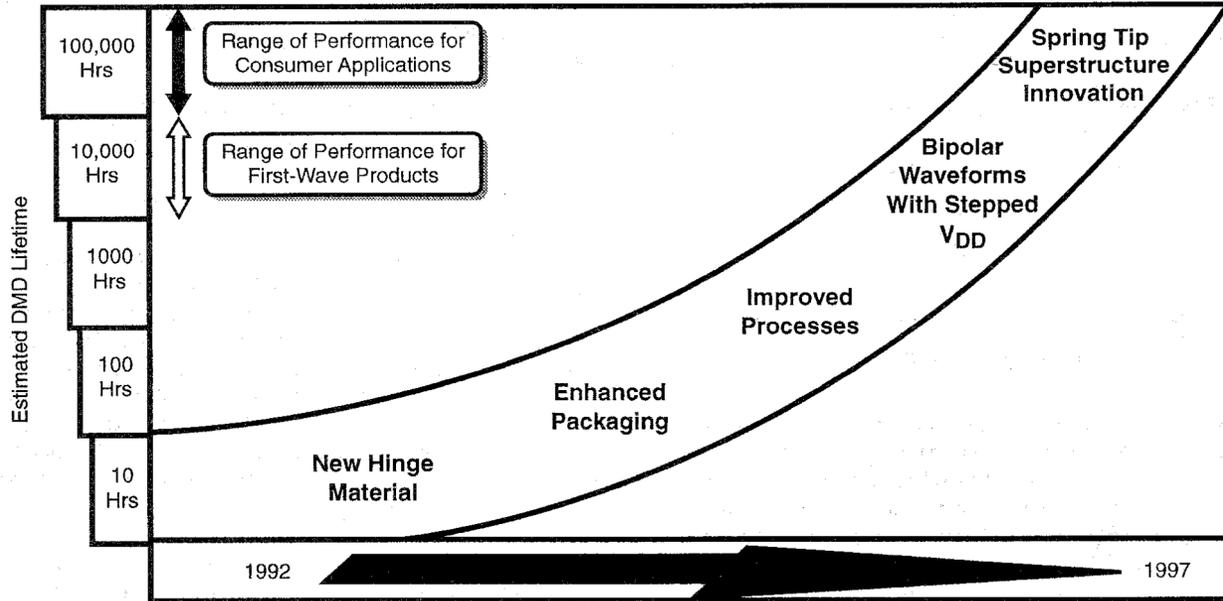
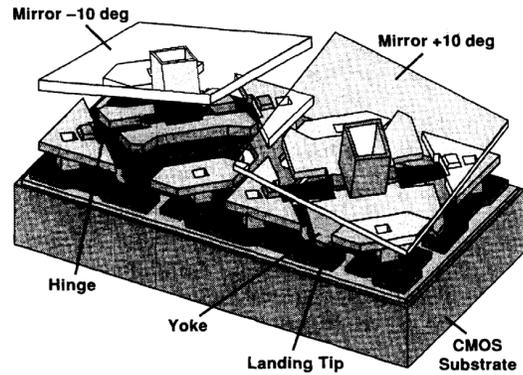
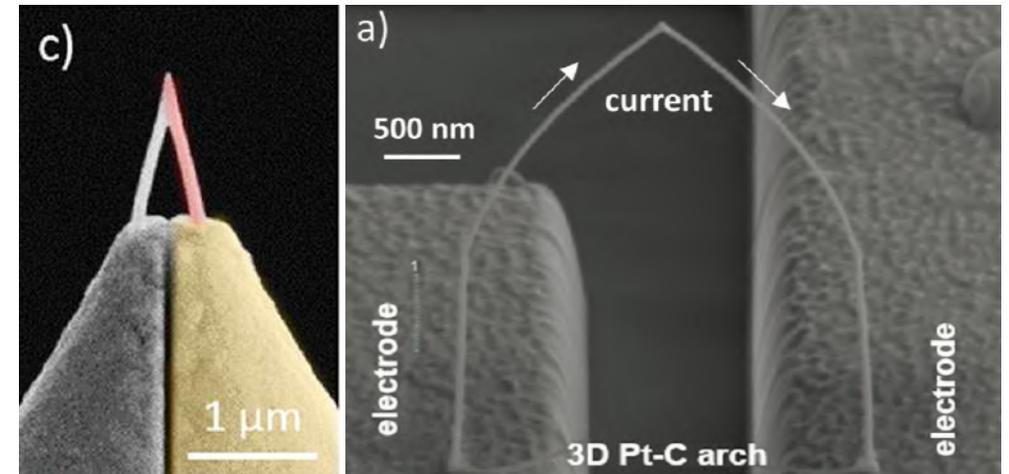
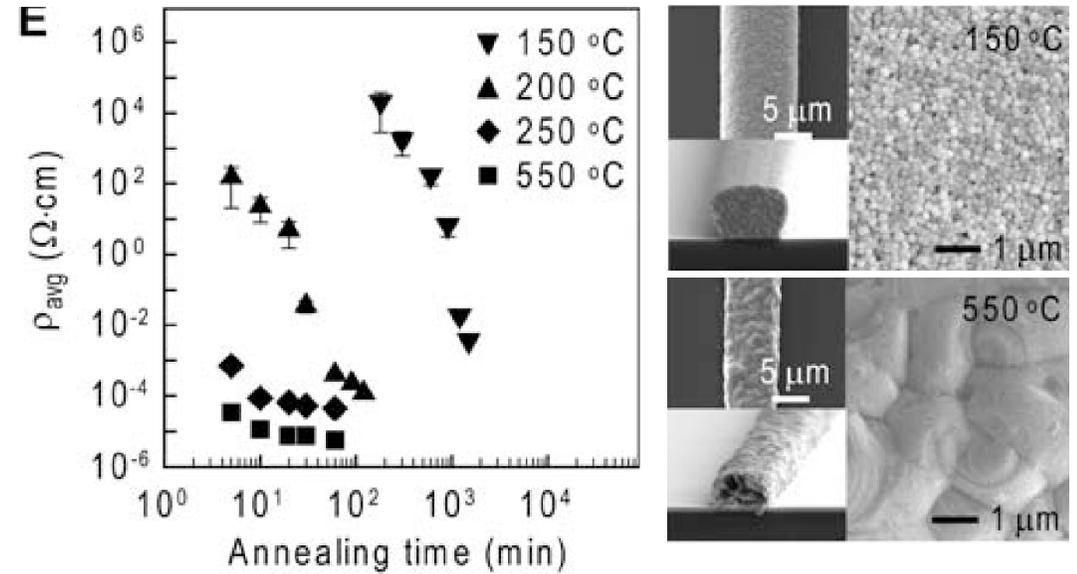
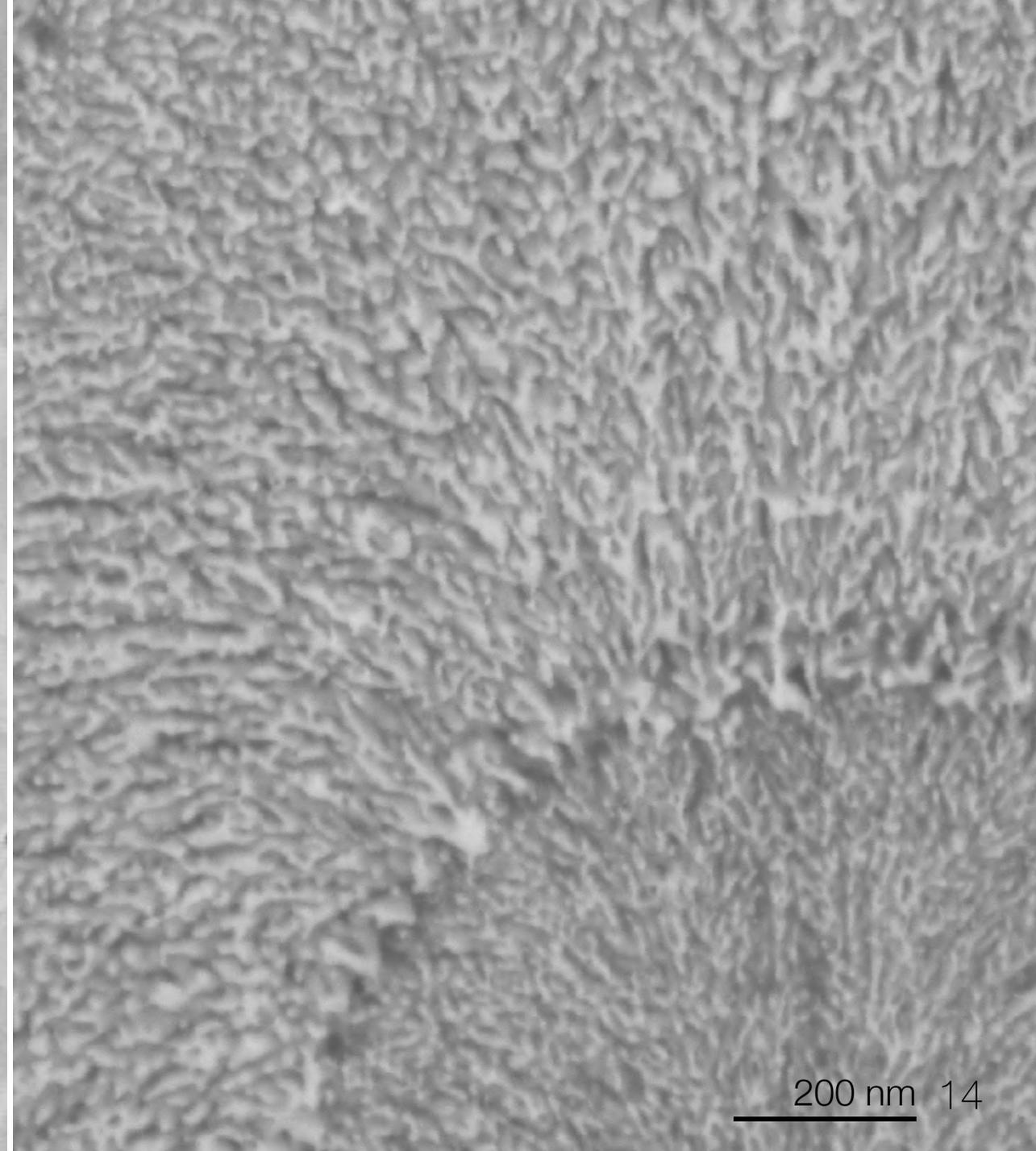
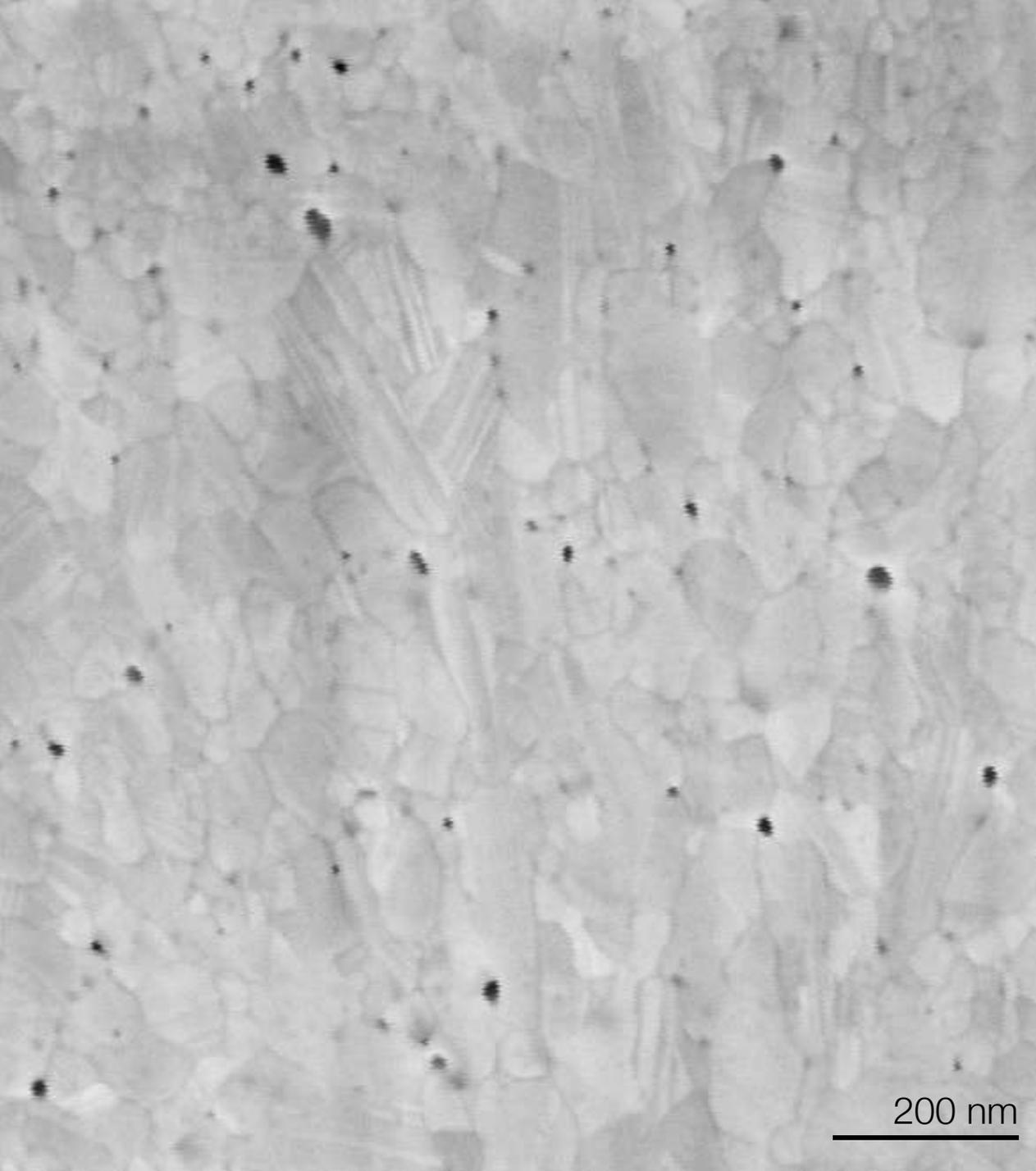
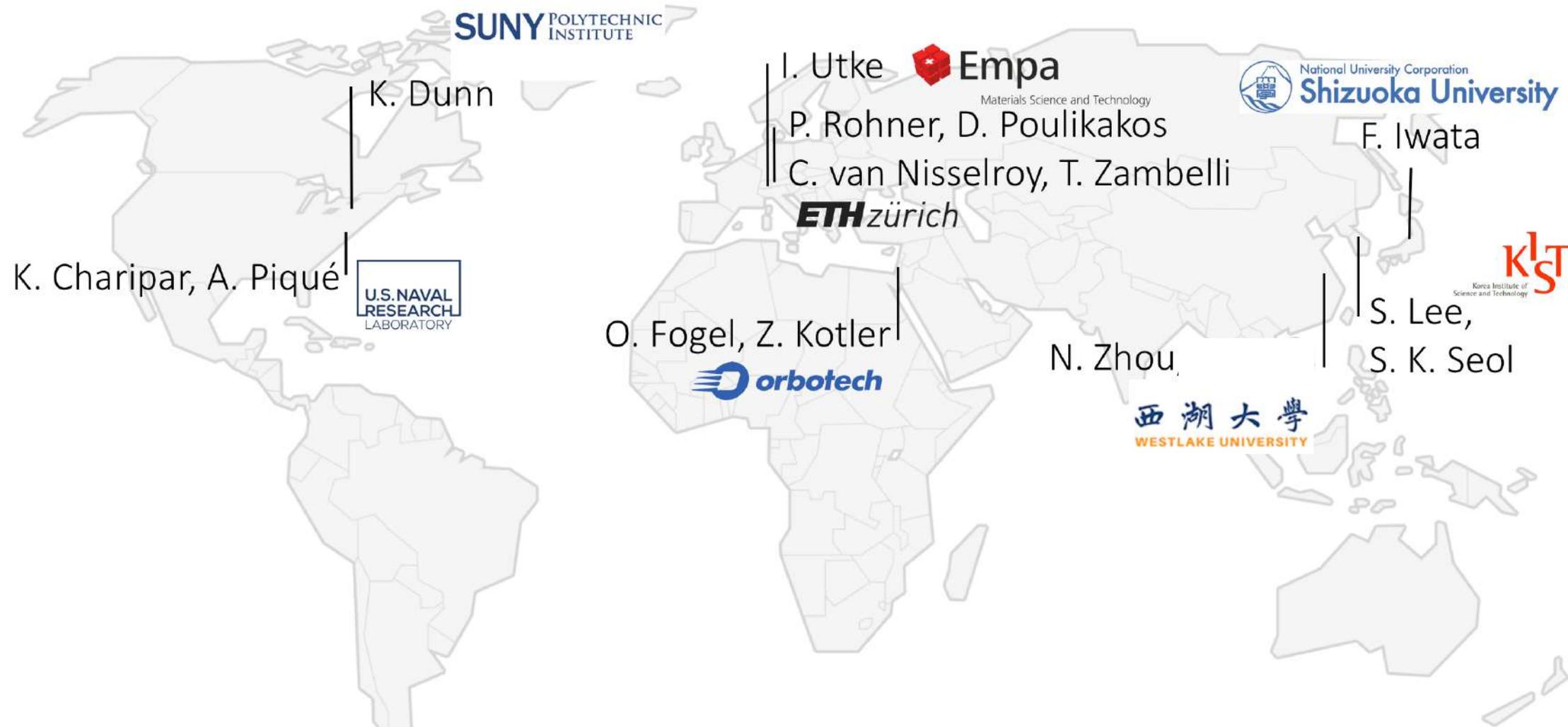


Figure 13. Reliability development and lifetime improvement





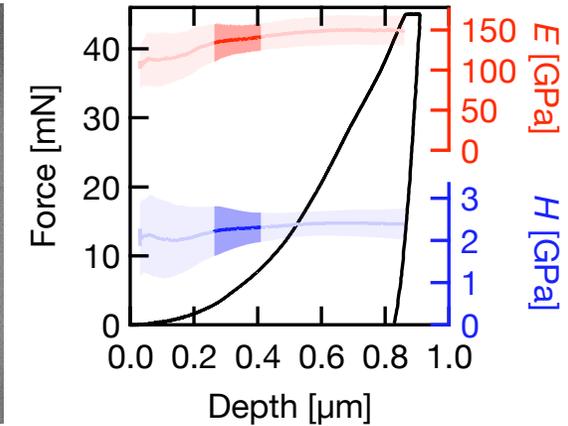
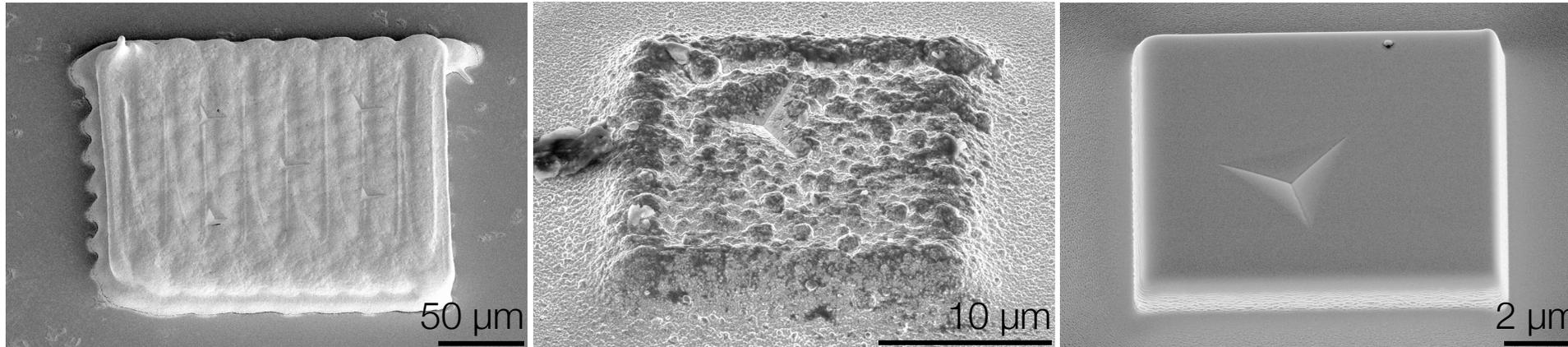
Our collaborators



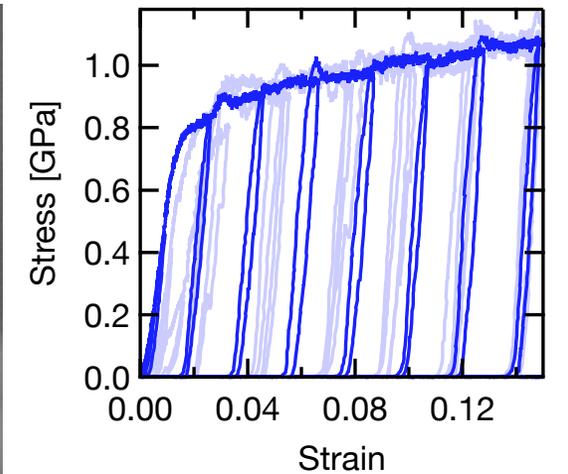
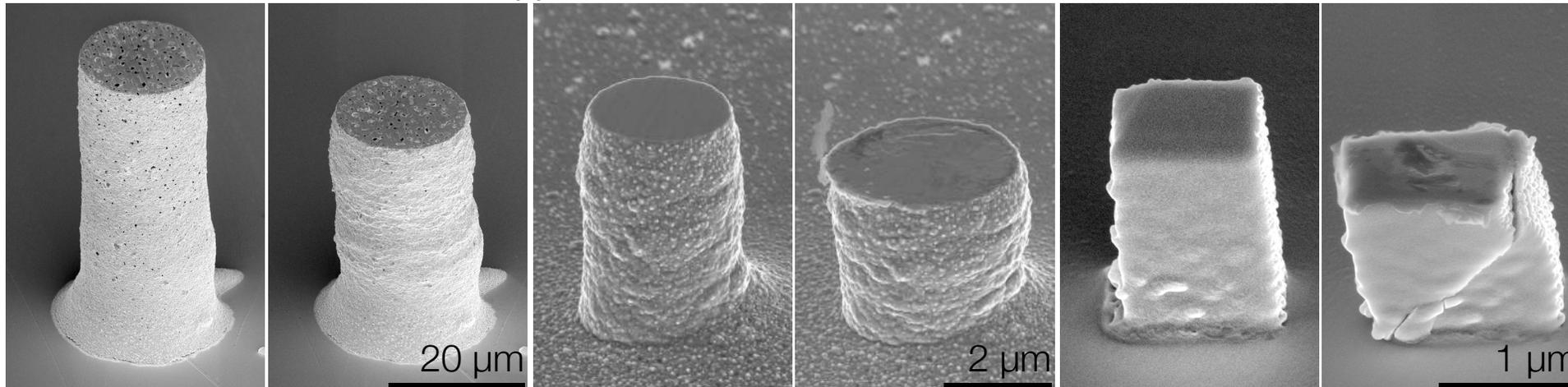
https://commons.wikimedia.org/wiki/Maps_of_the_world

Experimental: standardized set of samples for all techniques

Nanoindentation: E and H

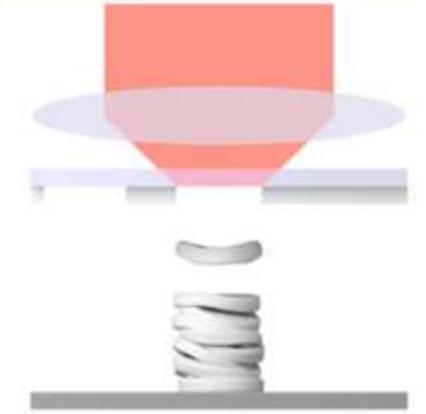
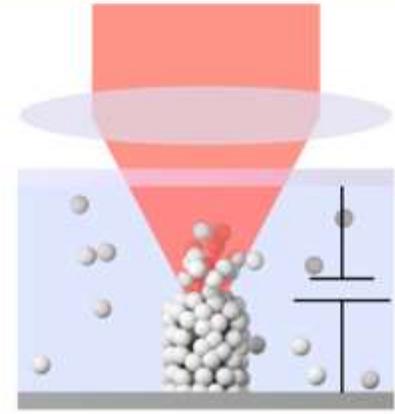
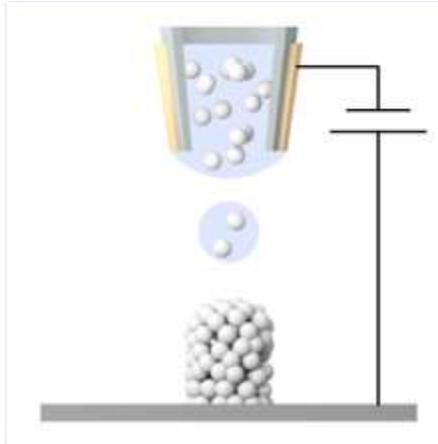


Microcompression: E and $\sigma_{0.07}$

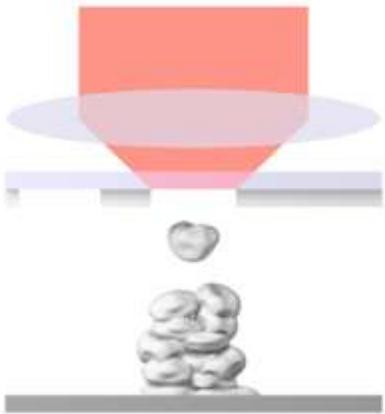


Methods for AM of metals at small scales (<math><10\ \mu\text{m}</math>)*

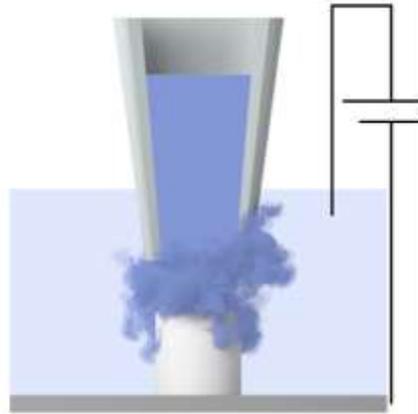
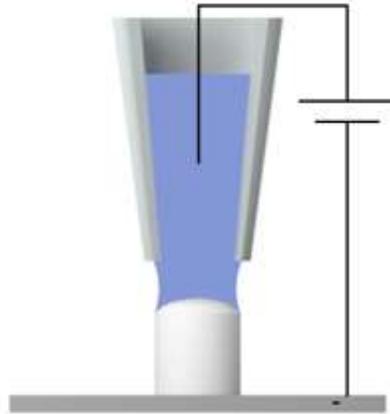
Transfer: colloids



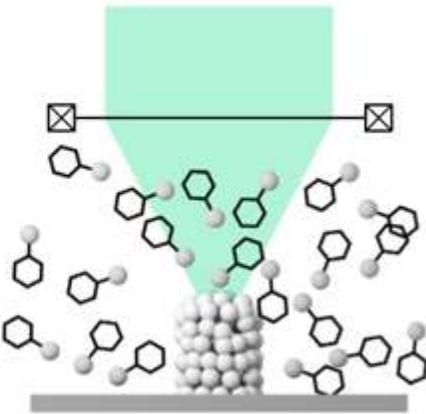
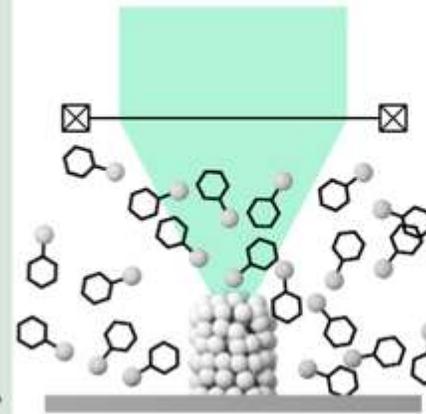
Transfer: melt



Synthesis: el. chemical



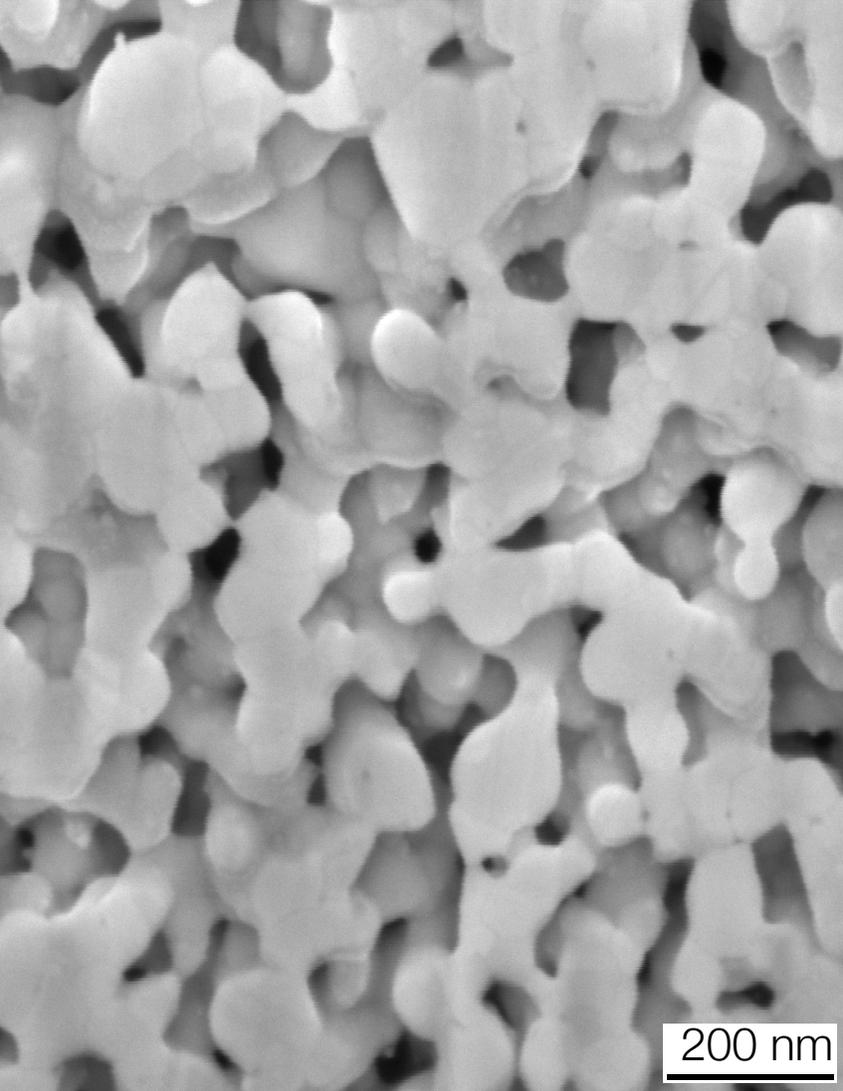
Synthesis: el.-ind. CVD



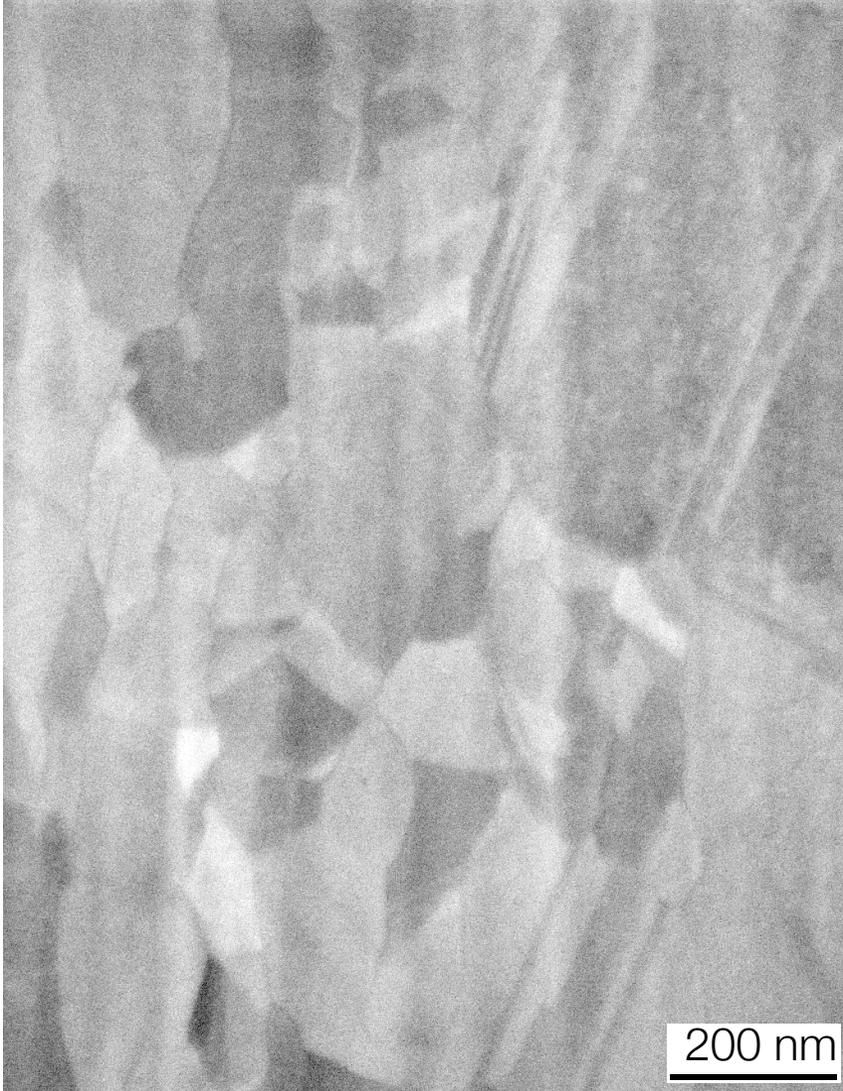
*Reiser, A., Hirt, L., Spolenak, R. & Zambelli, T. Adv. Mater. 29, 1604211 (2017).

Microstructure: porous / dense / metal-carbon composite

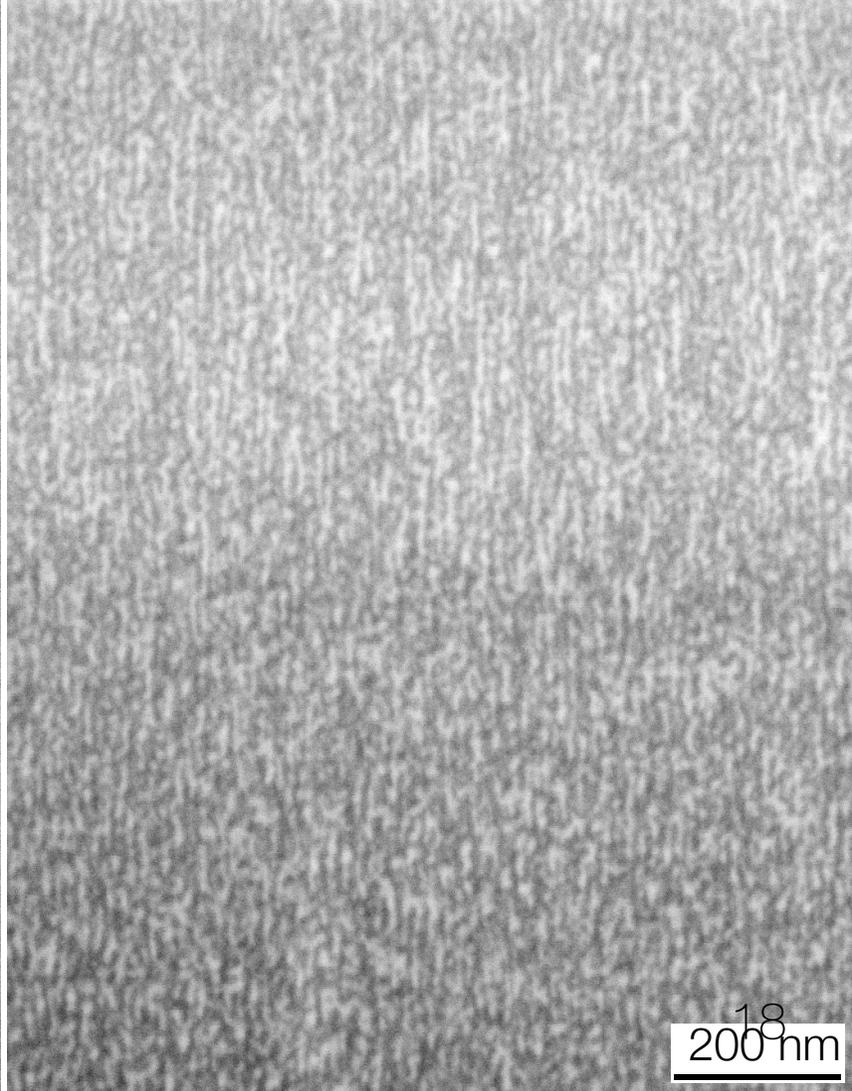
Transfer: colloids



Synthesis: electrochemical

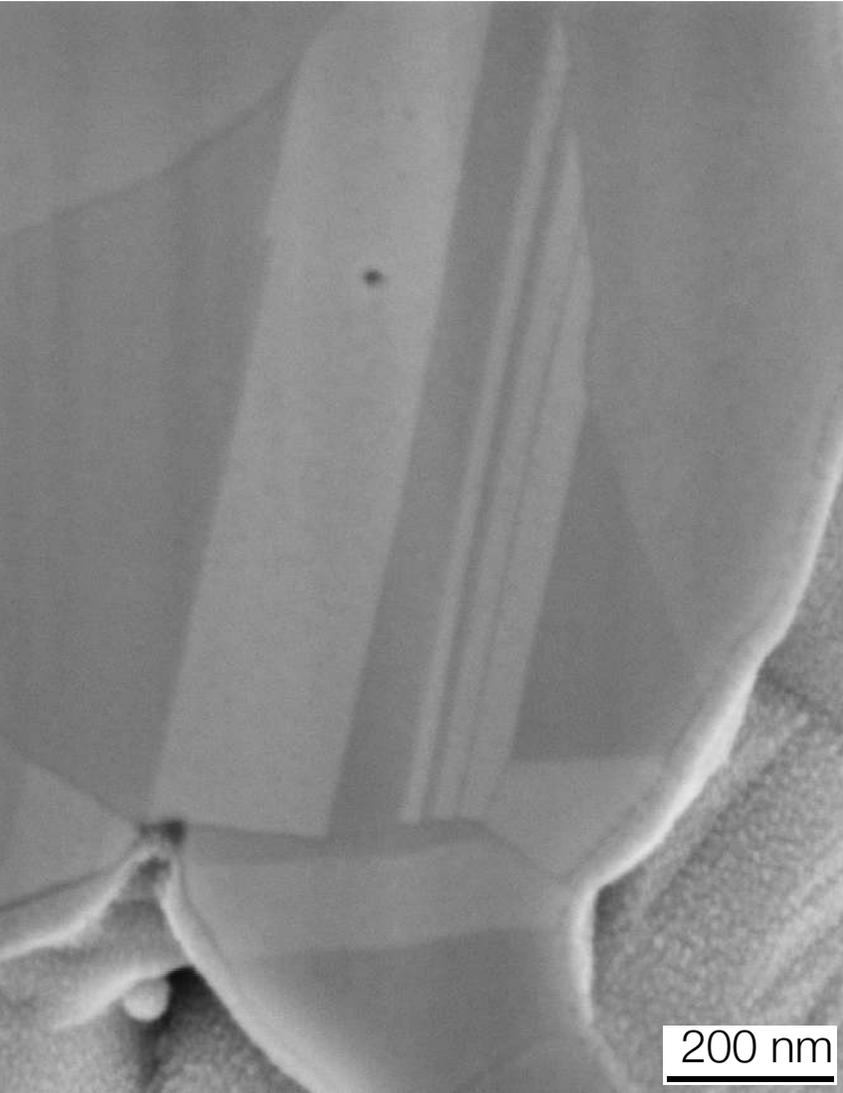


Synthesis: electron-induced CVD

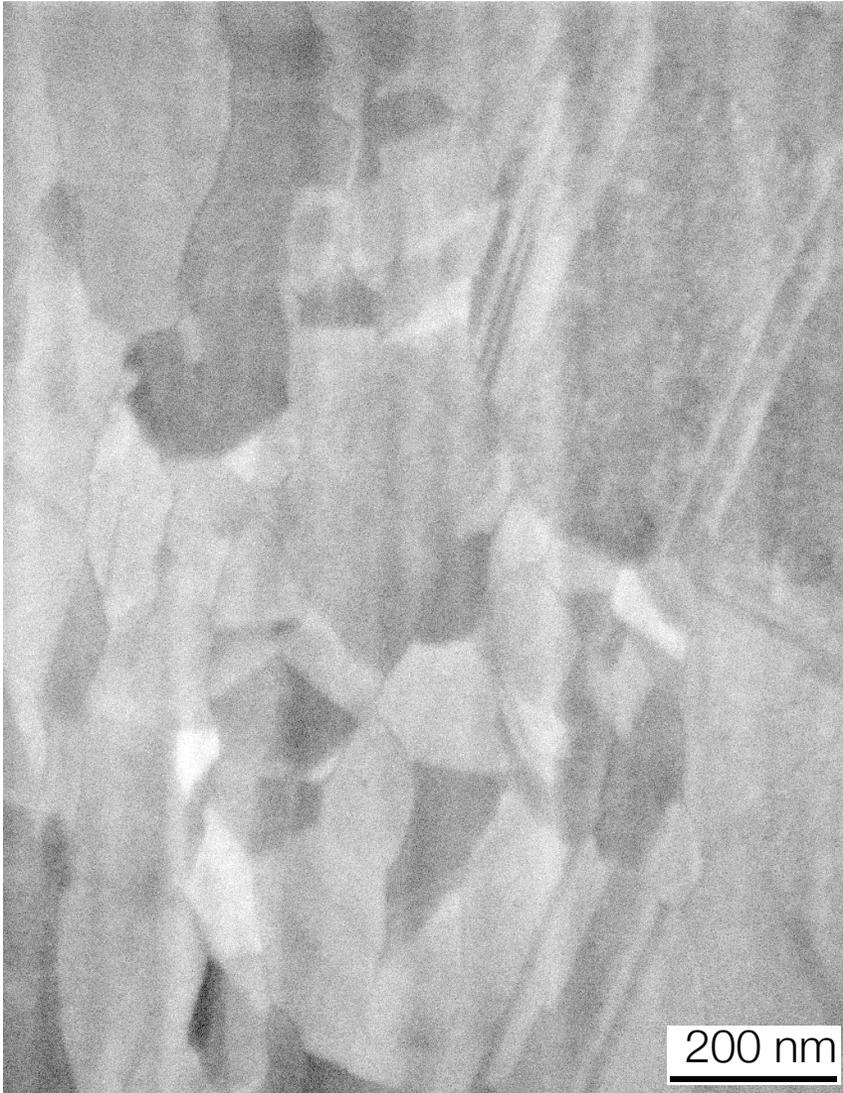


Microstructure: porous / dense / composite

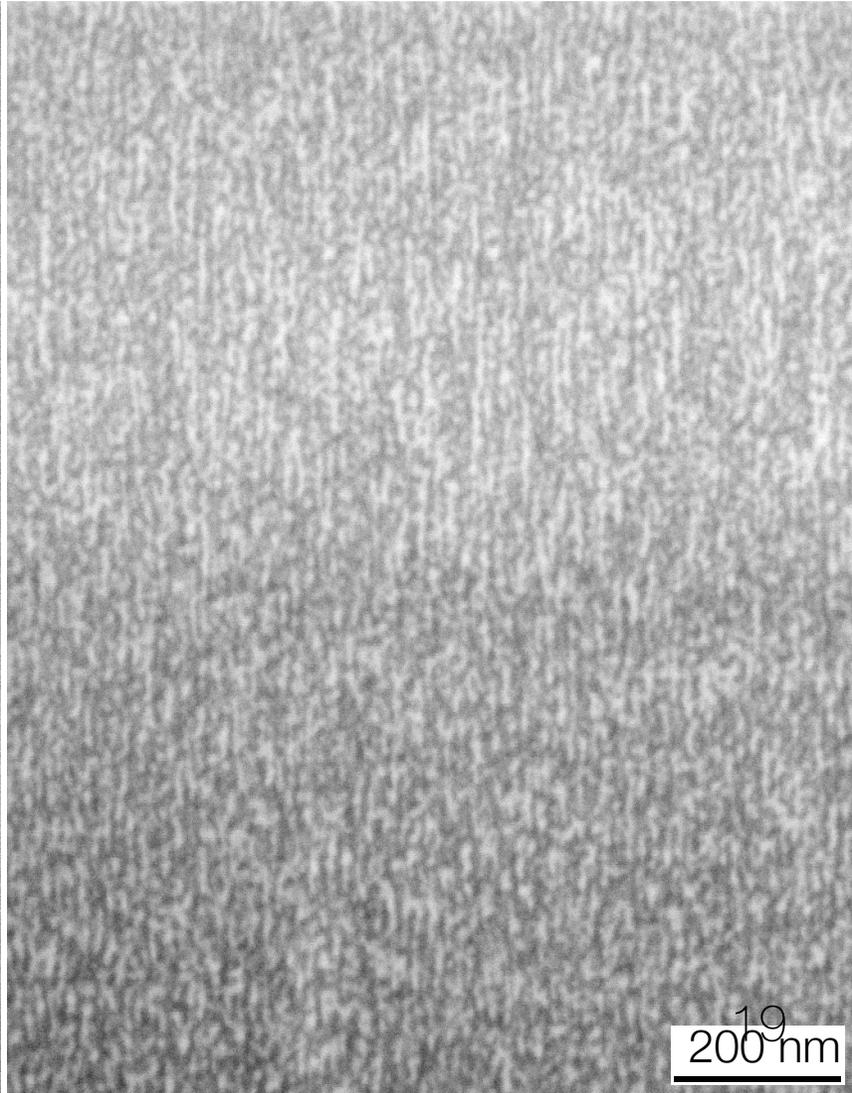
Transfer: colloids



Synthesis: electrochemical

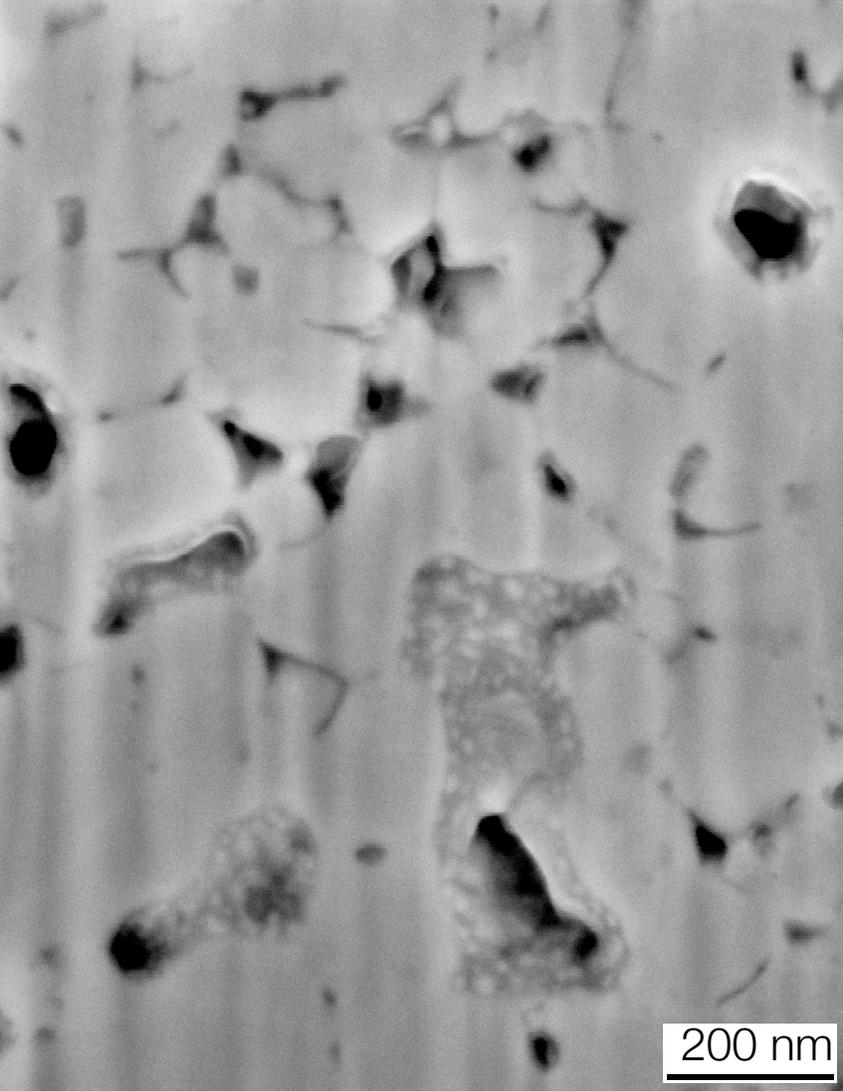


Synthesis: electron-induced CVD

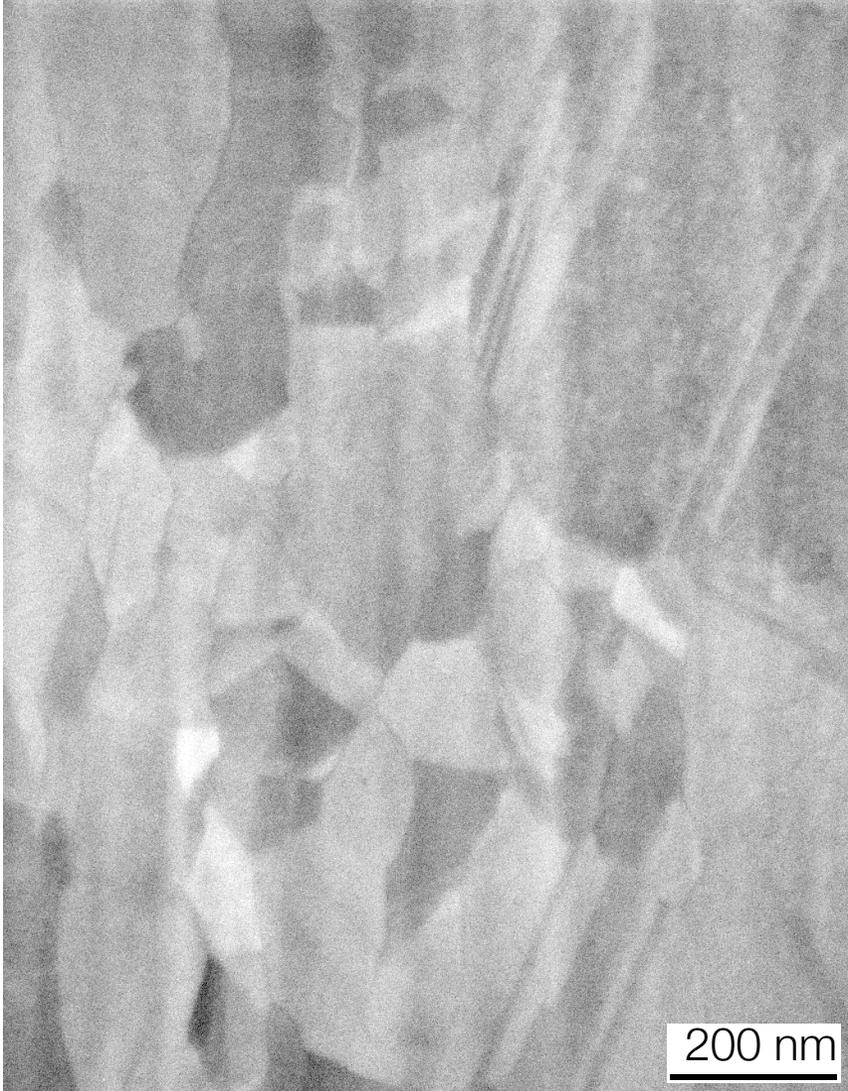


Microstructure: porous / dense / composite

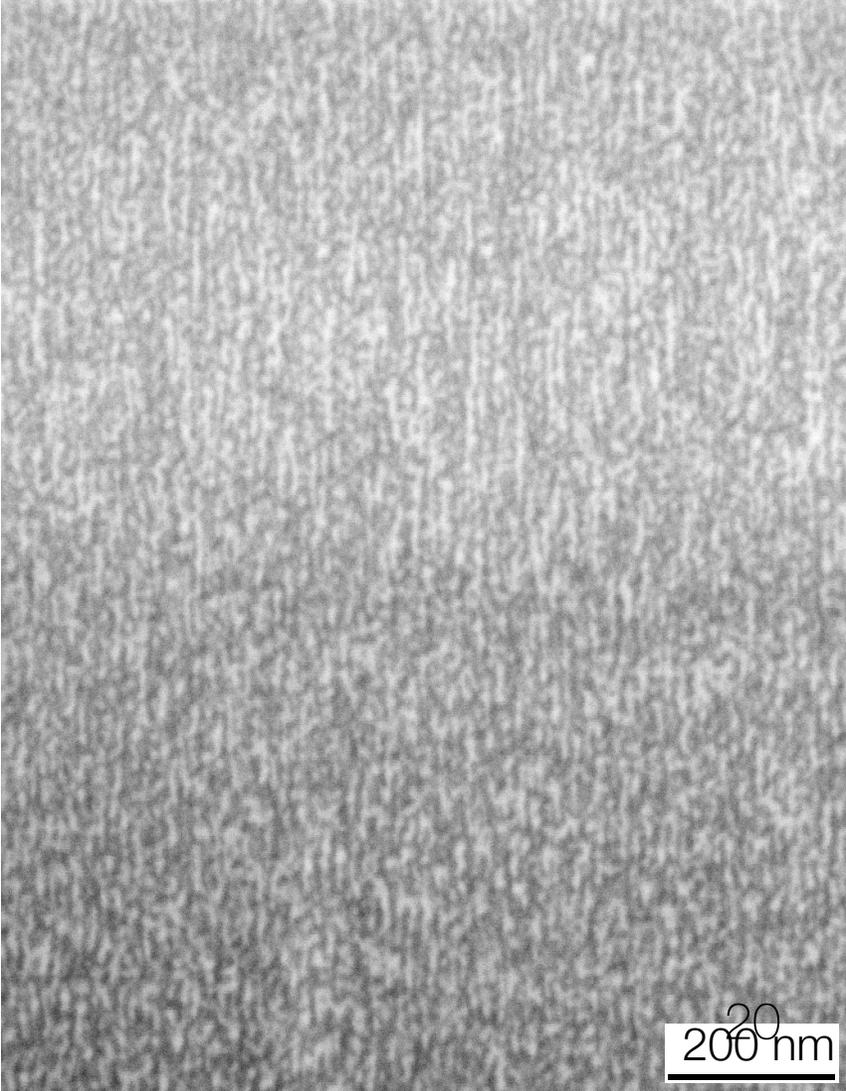
Transfer: colloids



Synthesis: electrochemical

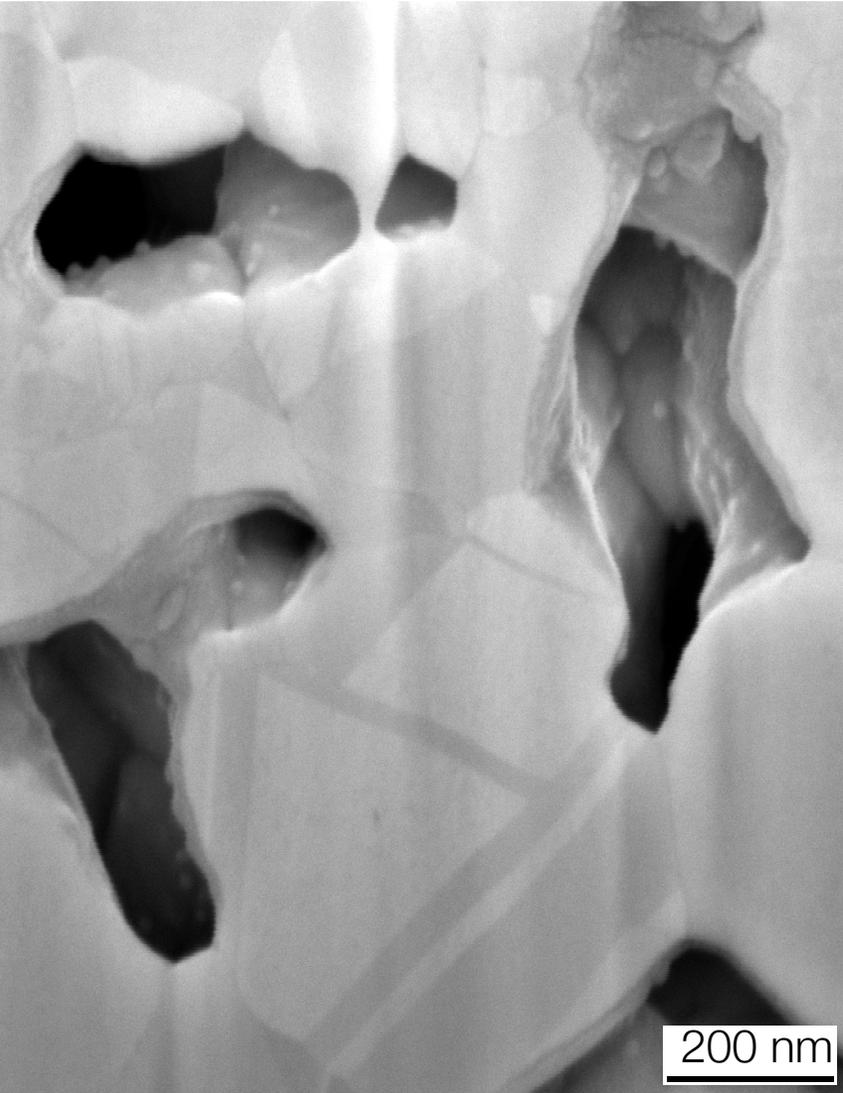


Synthesis: electron-induced CVD

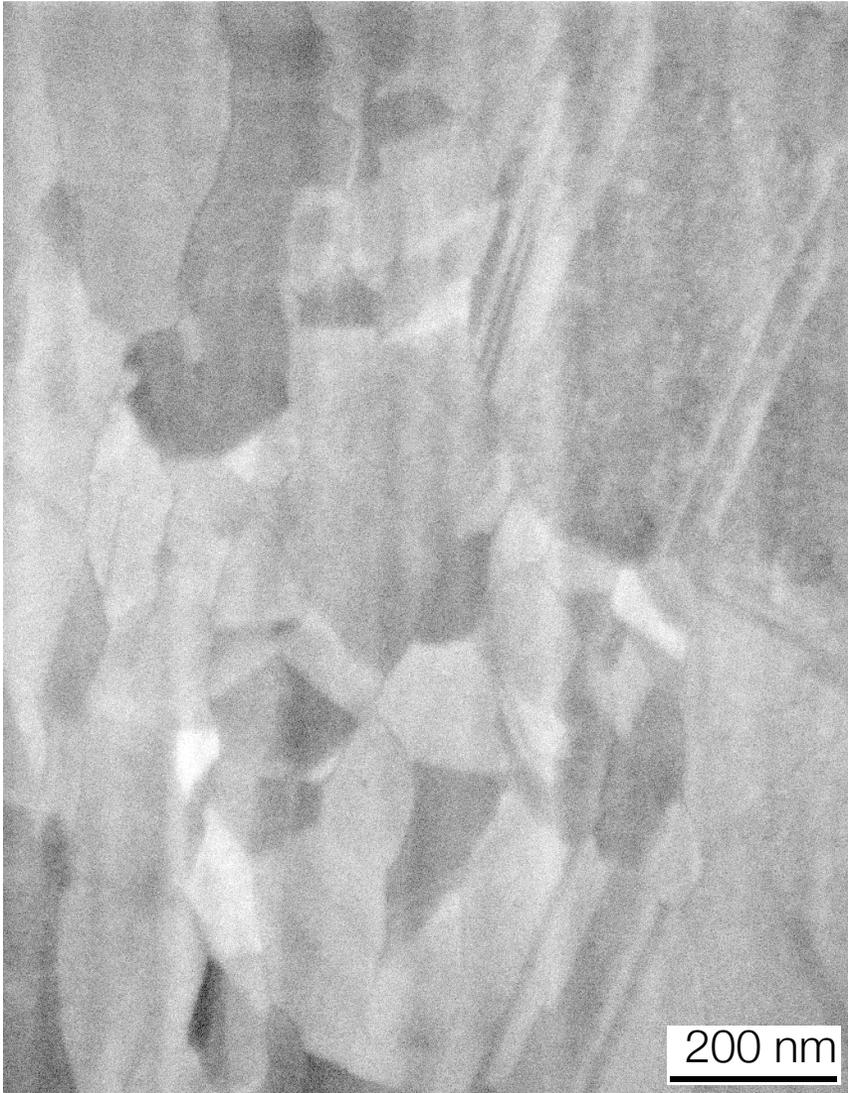


Microstructure: porous / dense / composite

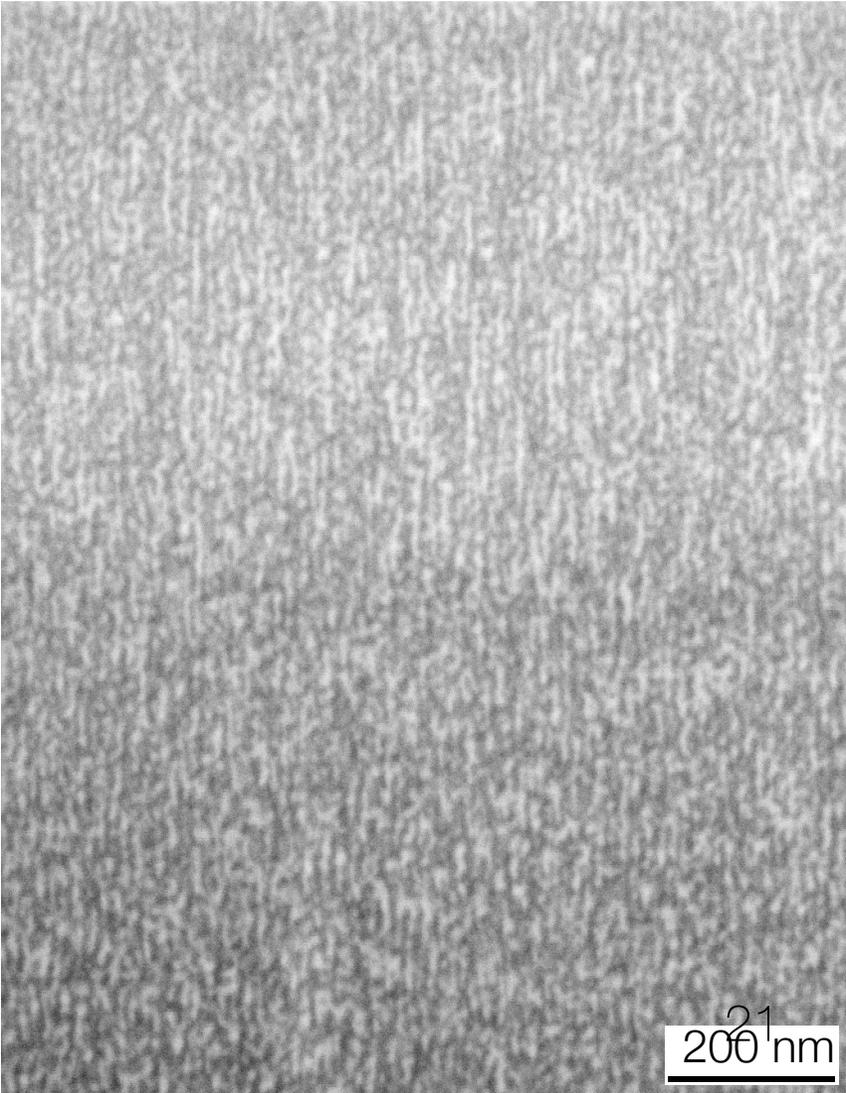
Transfer: colloids



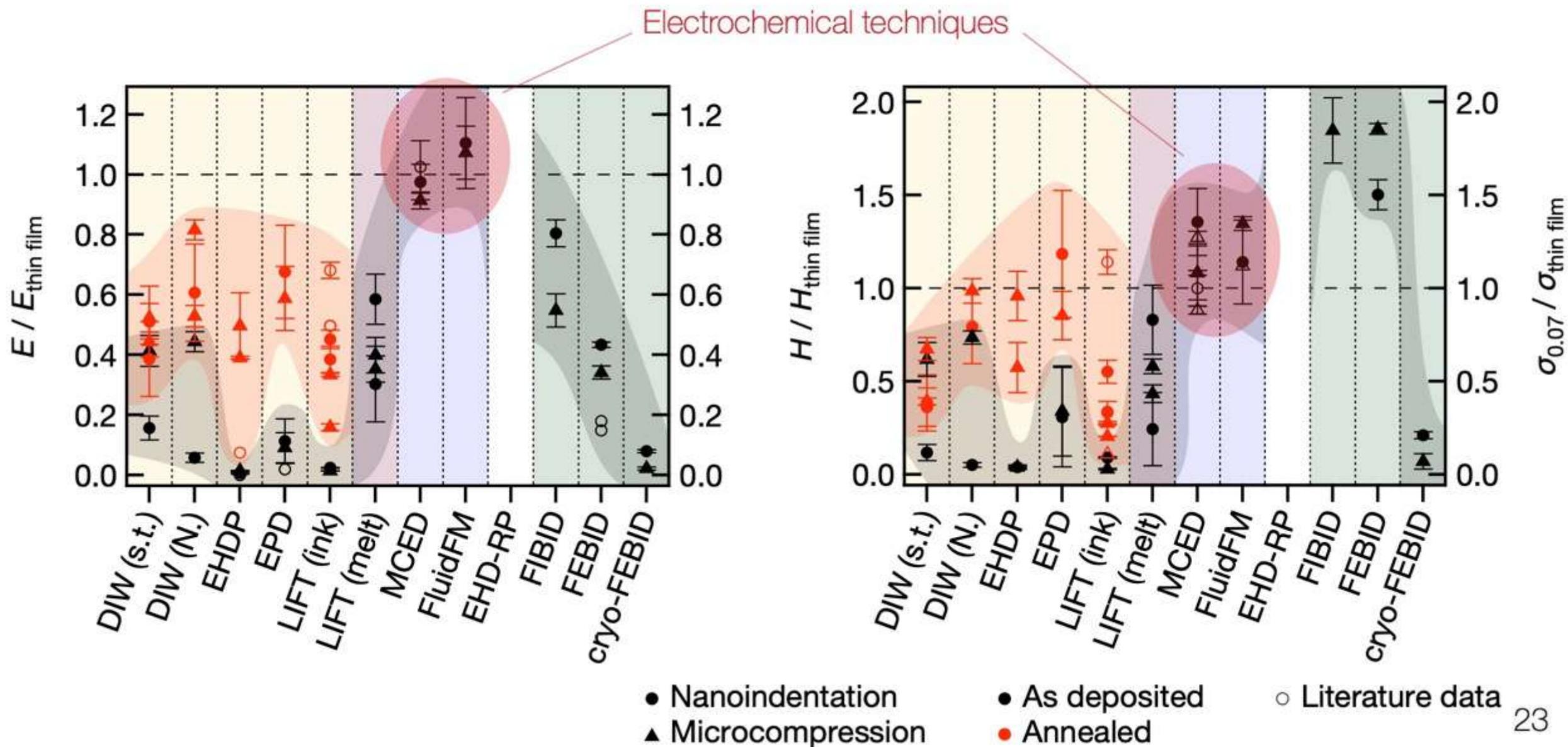
Synthesis: electrochemical



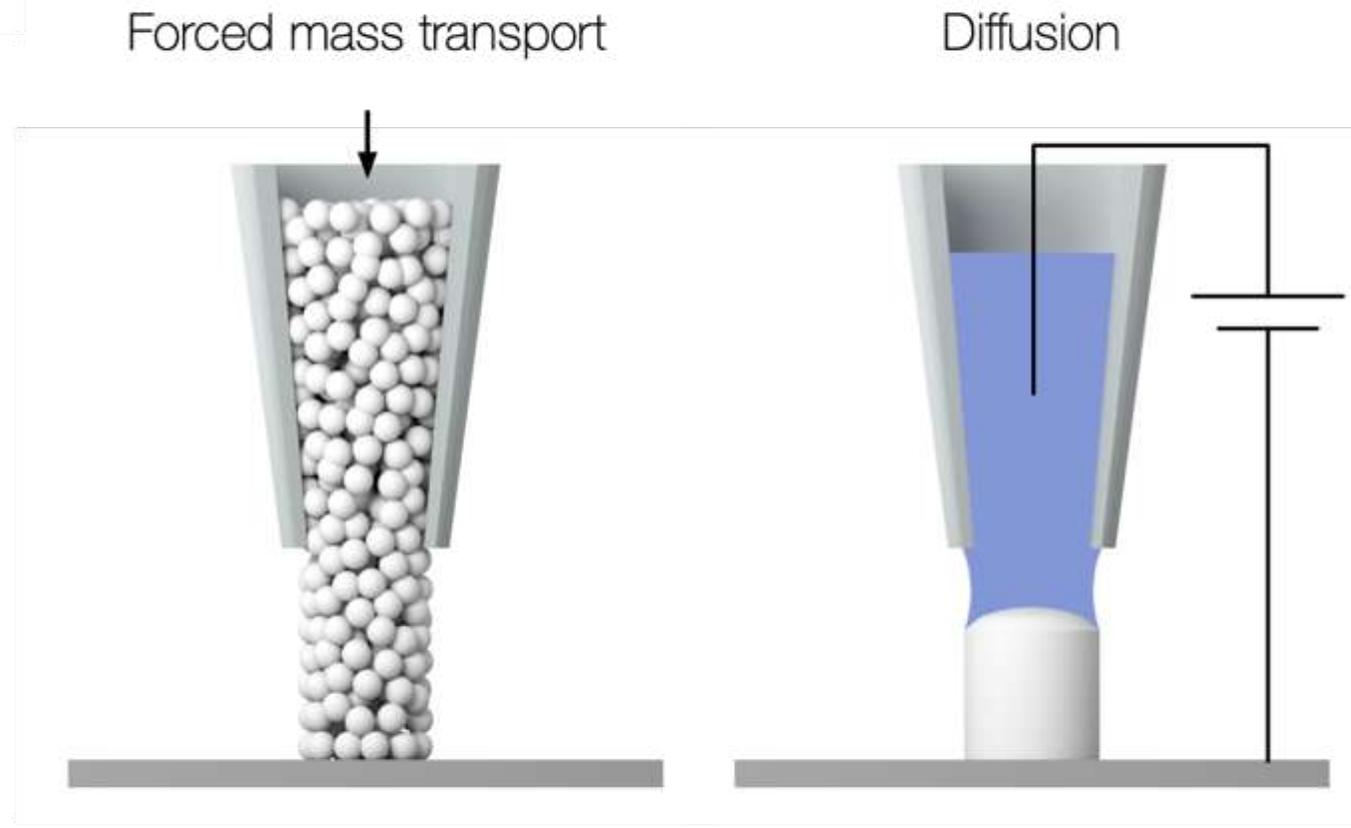
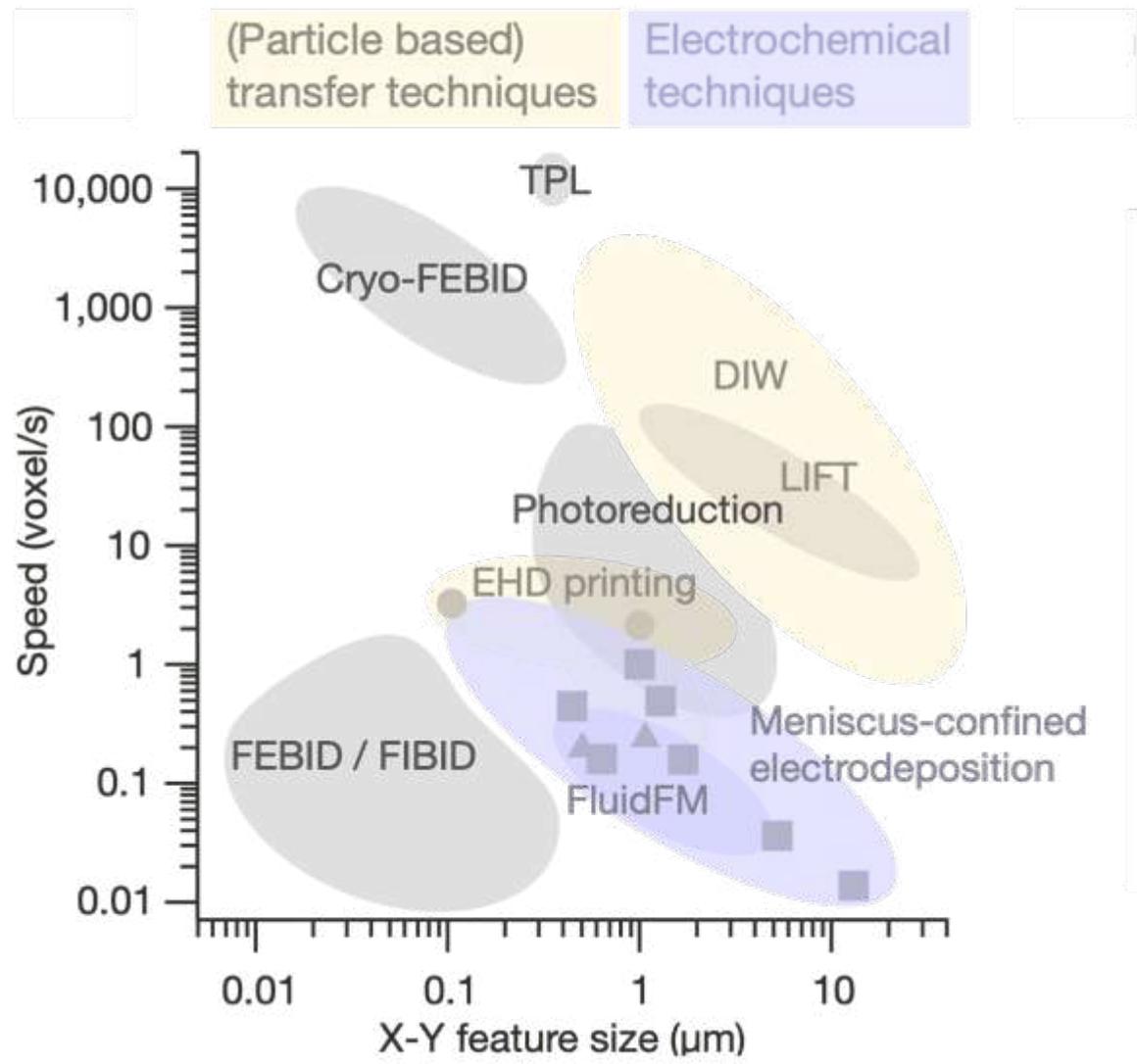
Synthesis: electron-induced CVD



Electrochemical techniques: best overall performance in terms of properties



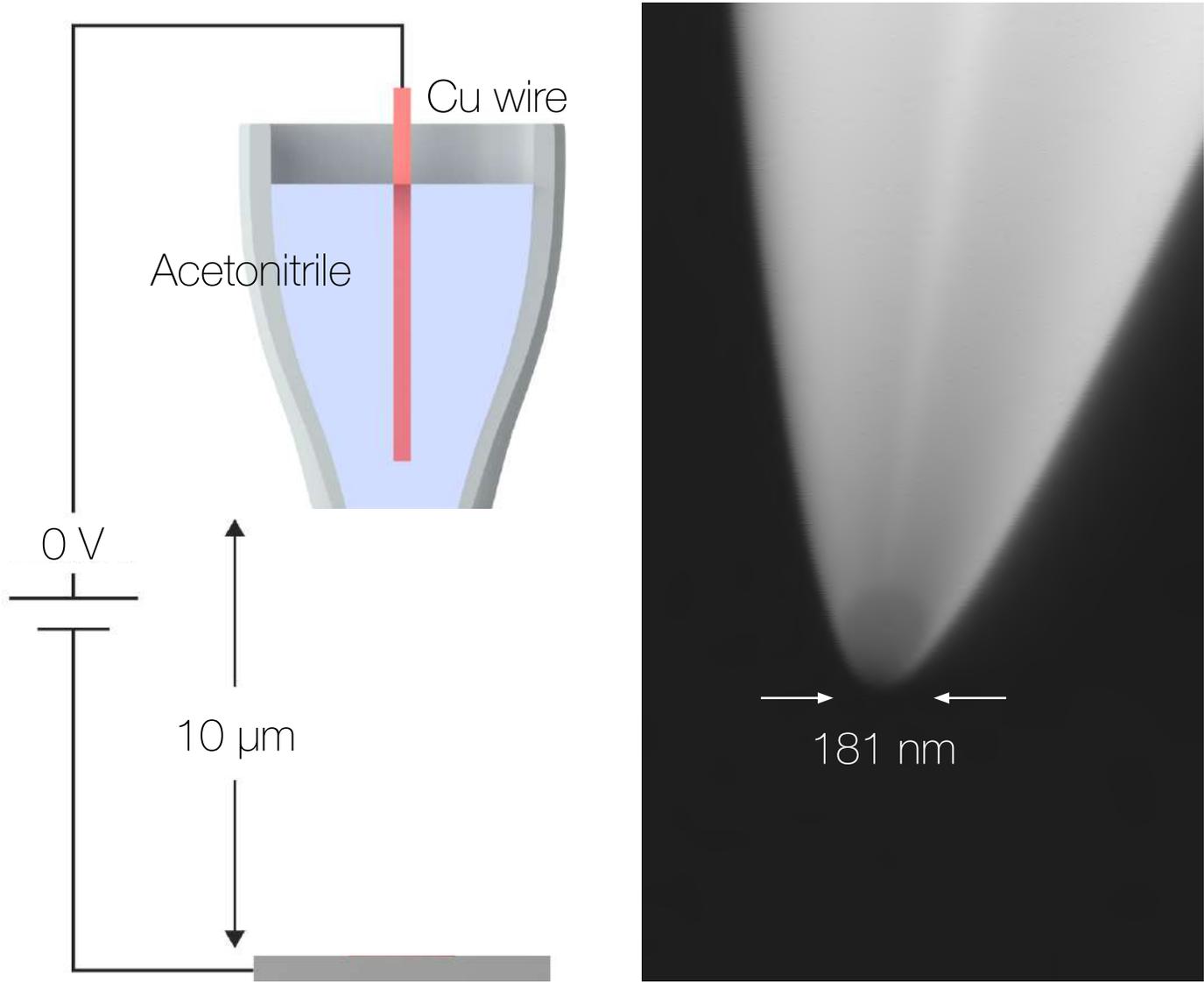
Electrochemical techniques: low speed due to mass-transport limitations



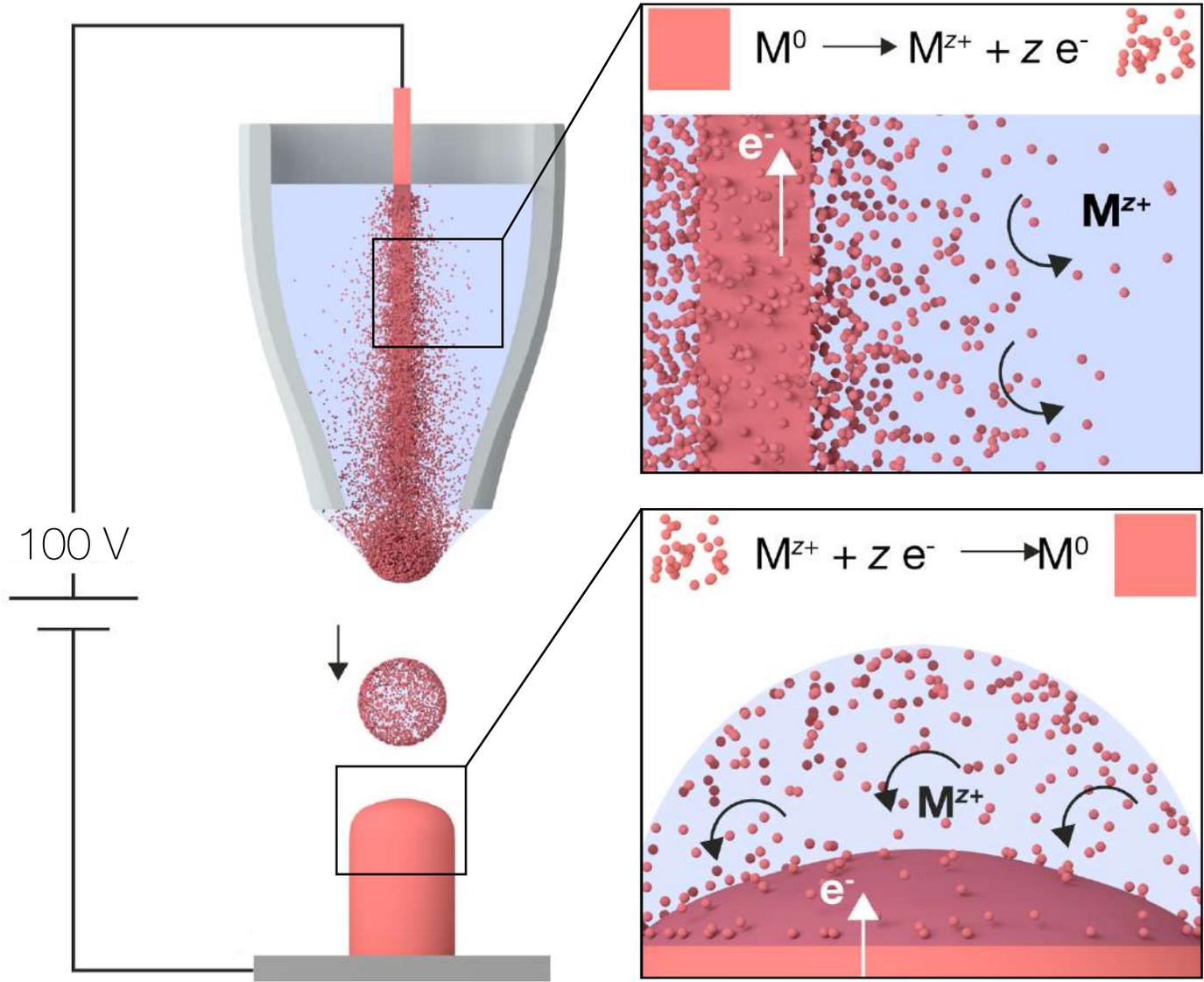
Part II: electrohydrodynamic redox printing (EHD-RP)*

*Reiser, A et al. Nature Commun. 10, 1853 (2019)

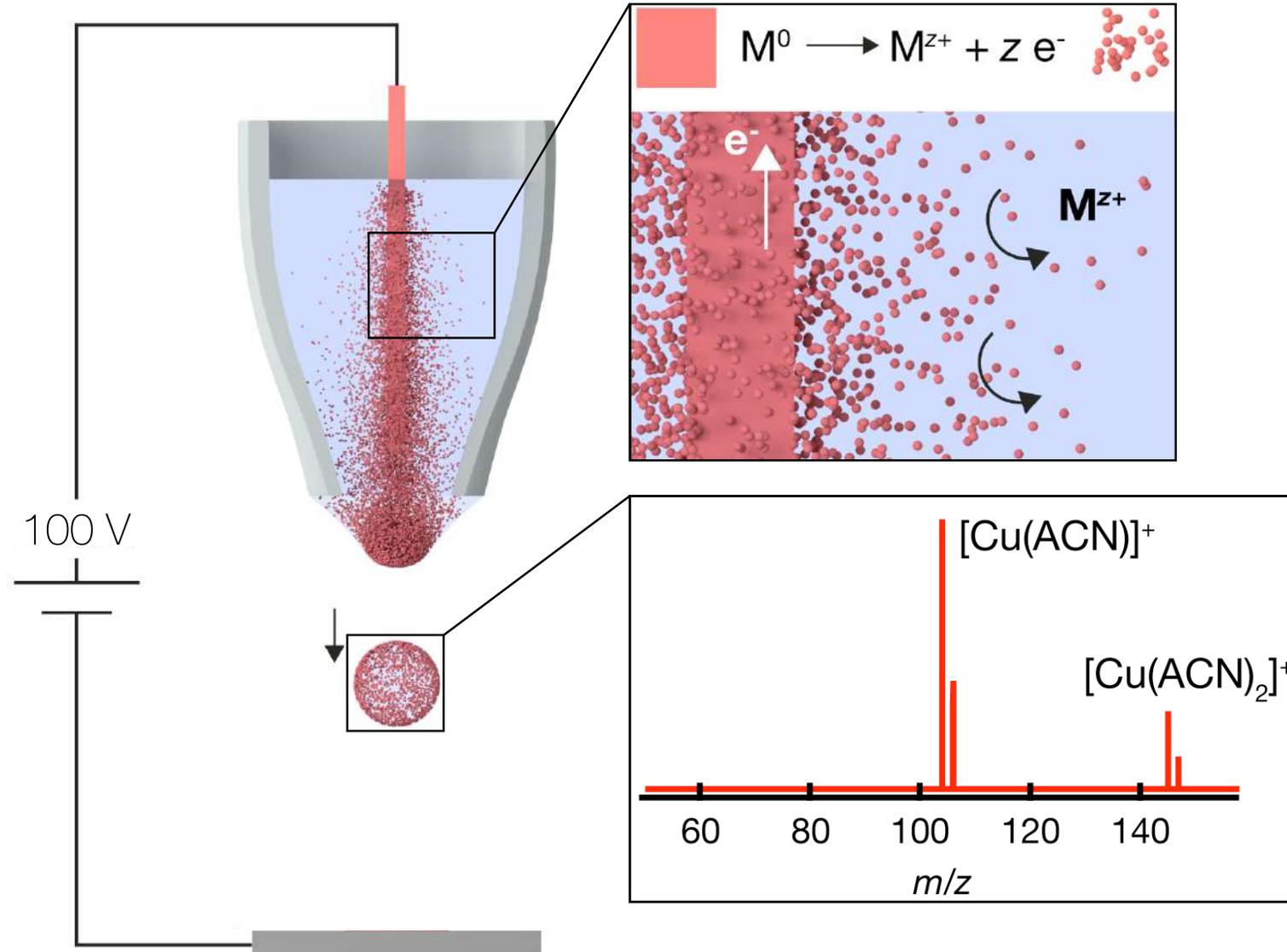
Electrohydrodynamic redox printing: dissolution of a sacrificial anode



Electrohydrodynamic redox printing

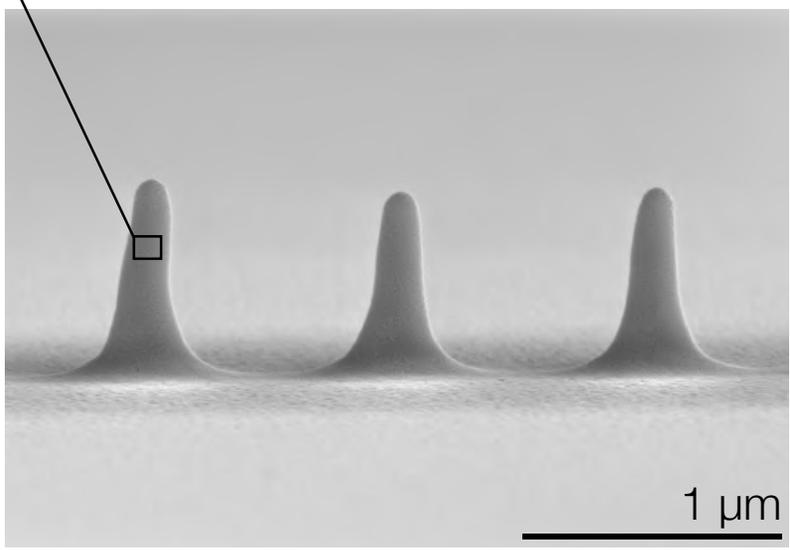
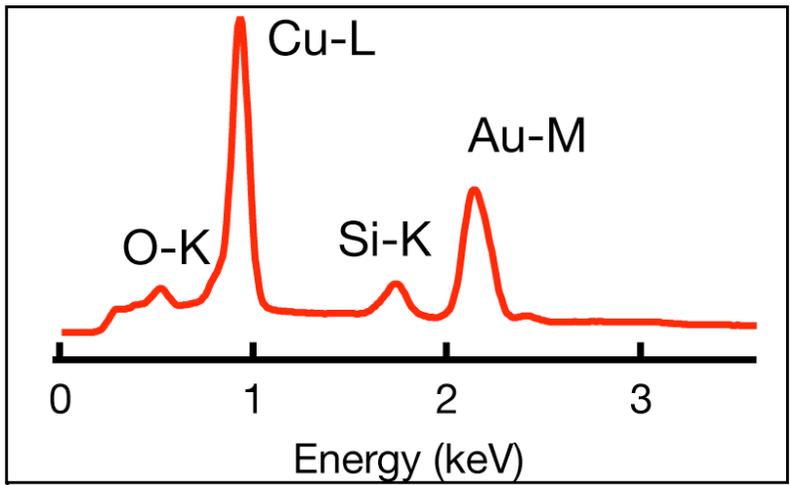
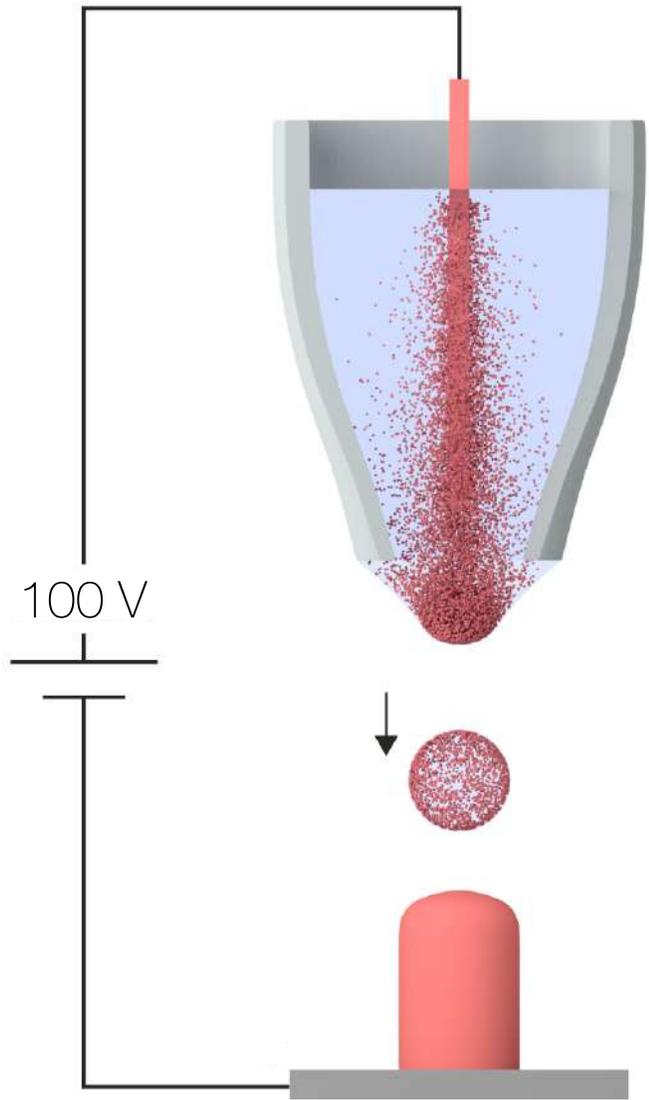


Electrohydrodynamic redox printing



ACN: Acetonitrile

Electrohydrodynamic redox printing



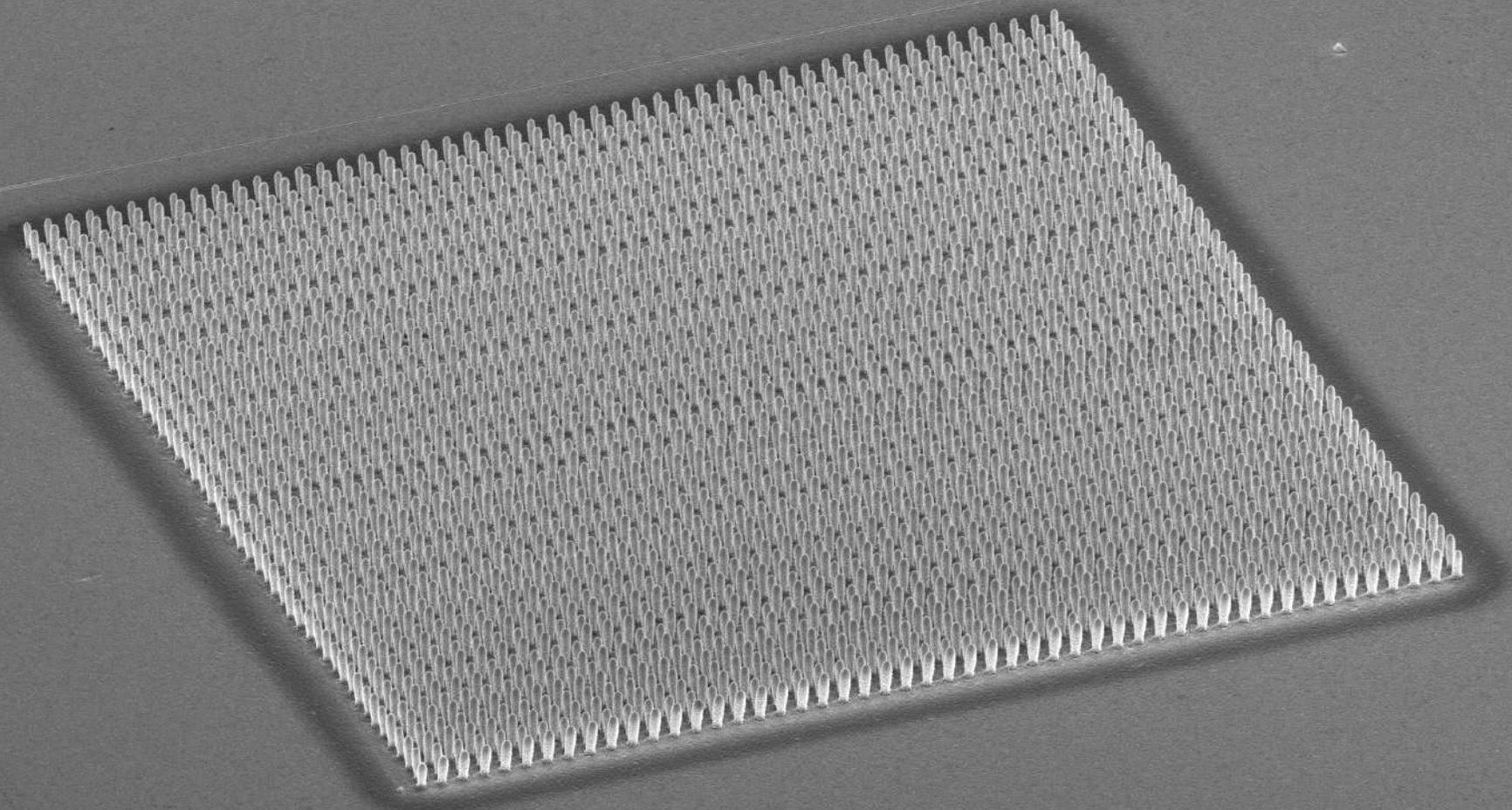
Video showing the printing process of diffraction grating of next slide

Please find it in the supplementary information of : *Reiser, A et al. Nature Commun. 10, 1853 (2019)*

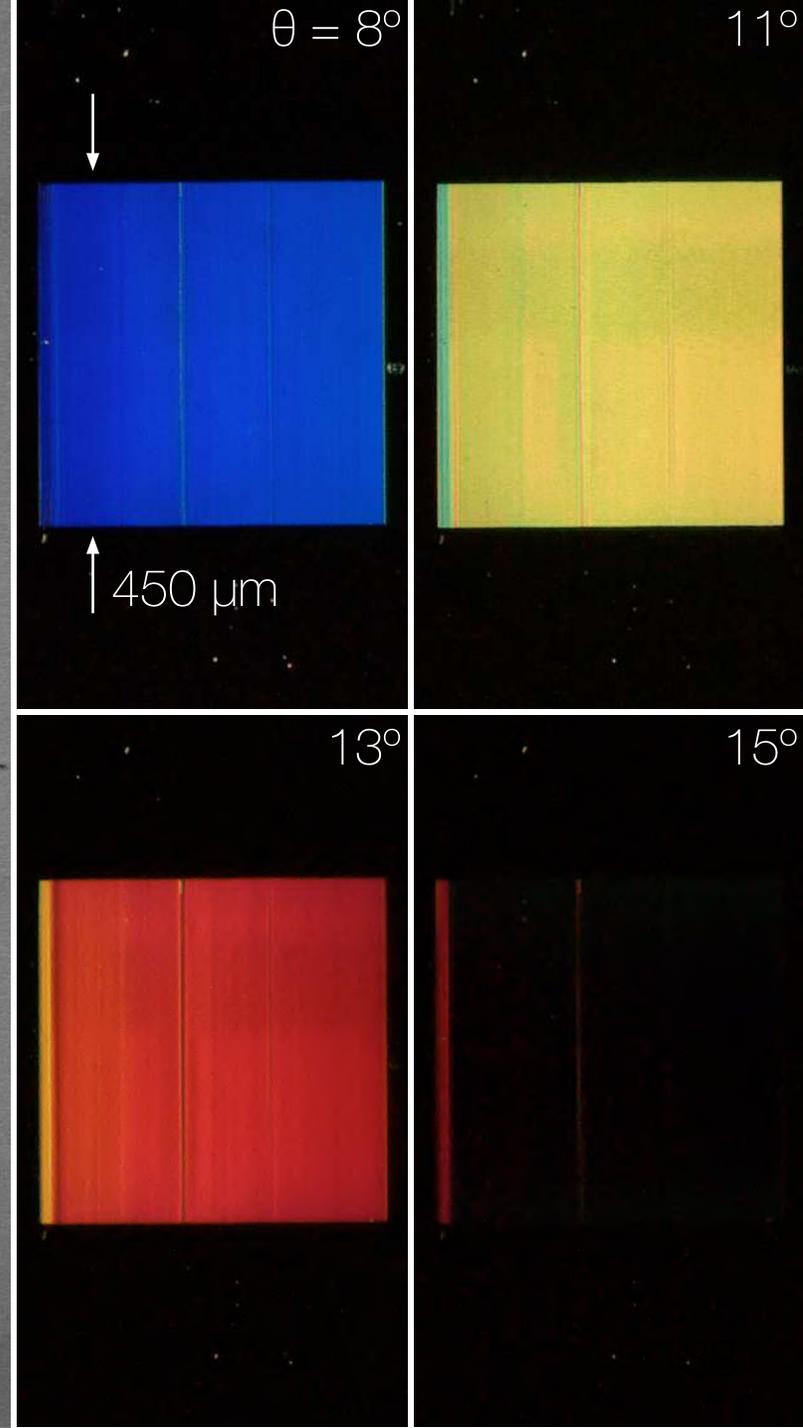
<https://www.nature.com/articles/s41467-019-09827-1#Sec13>

Supplementary Movie 2

High speed



5 μm



$\theta = 8^\circ$

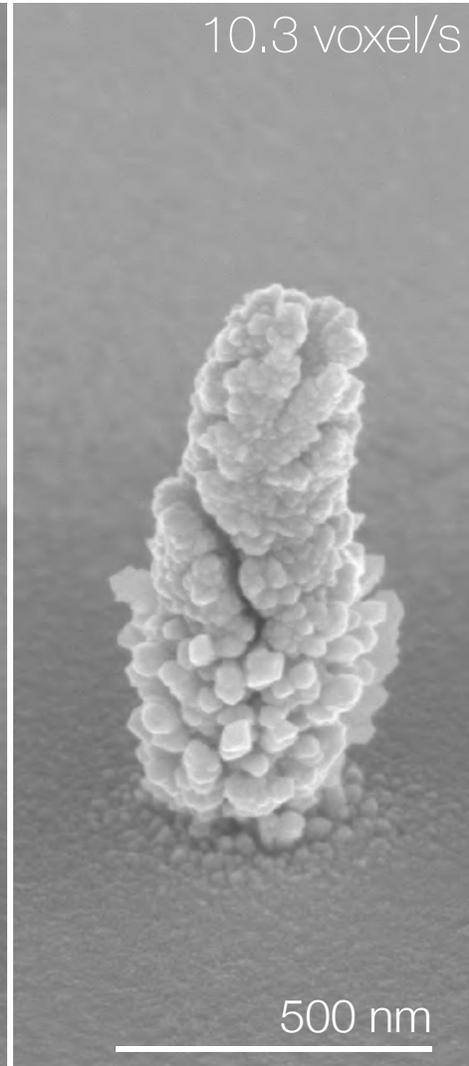
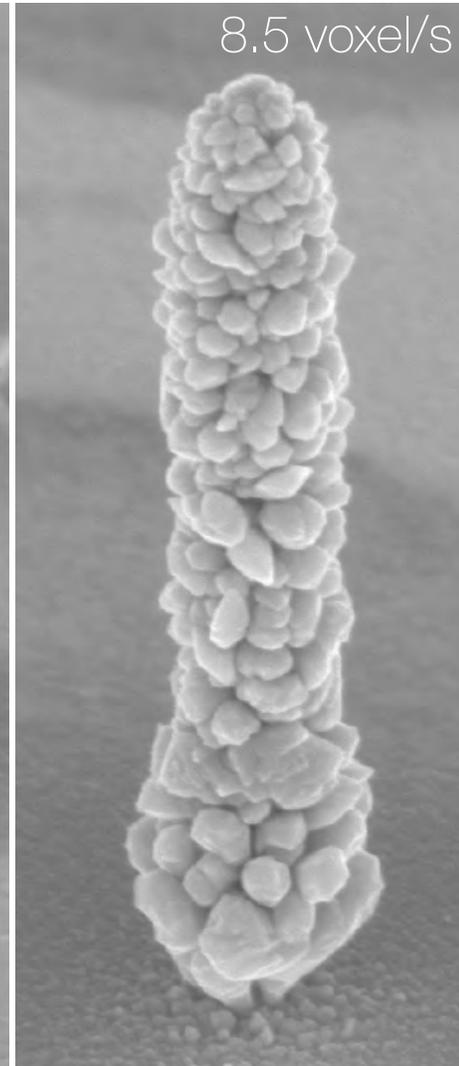
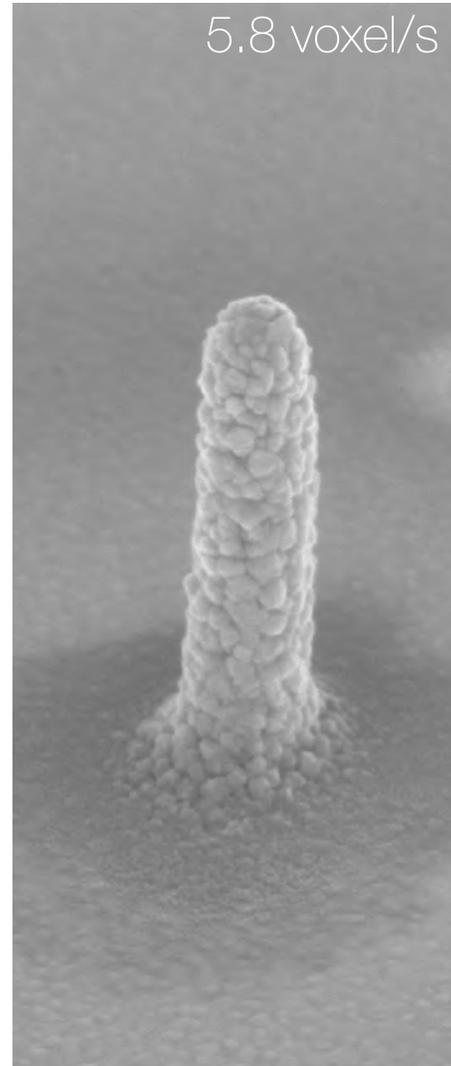
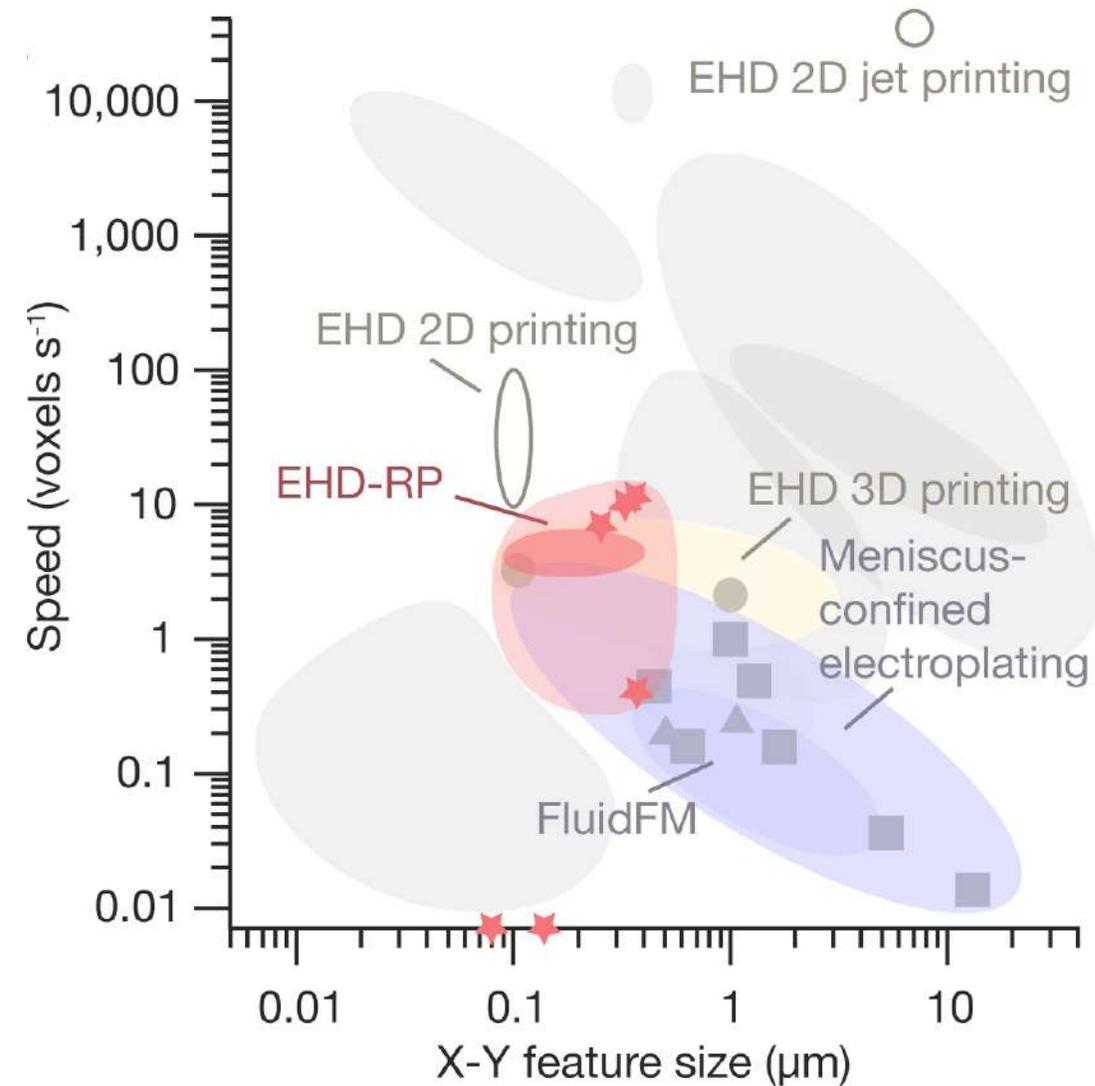
11°

13°

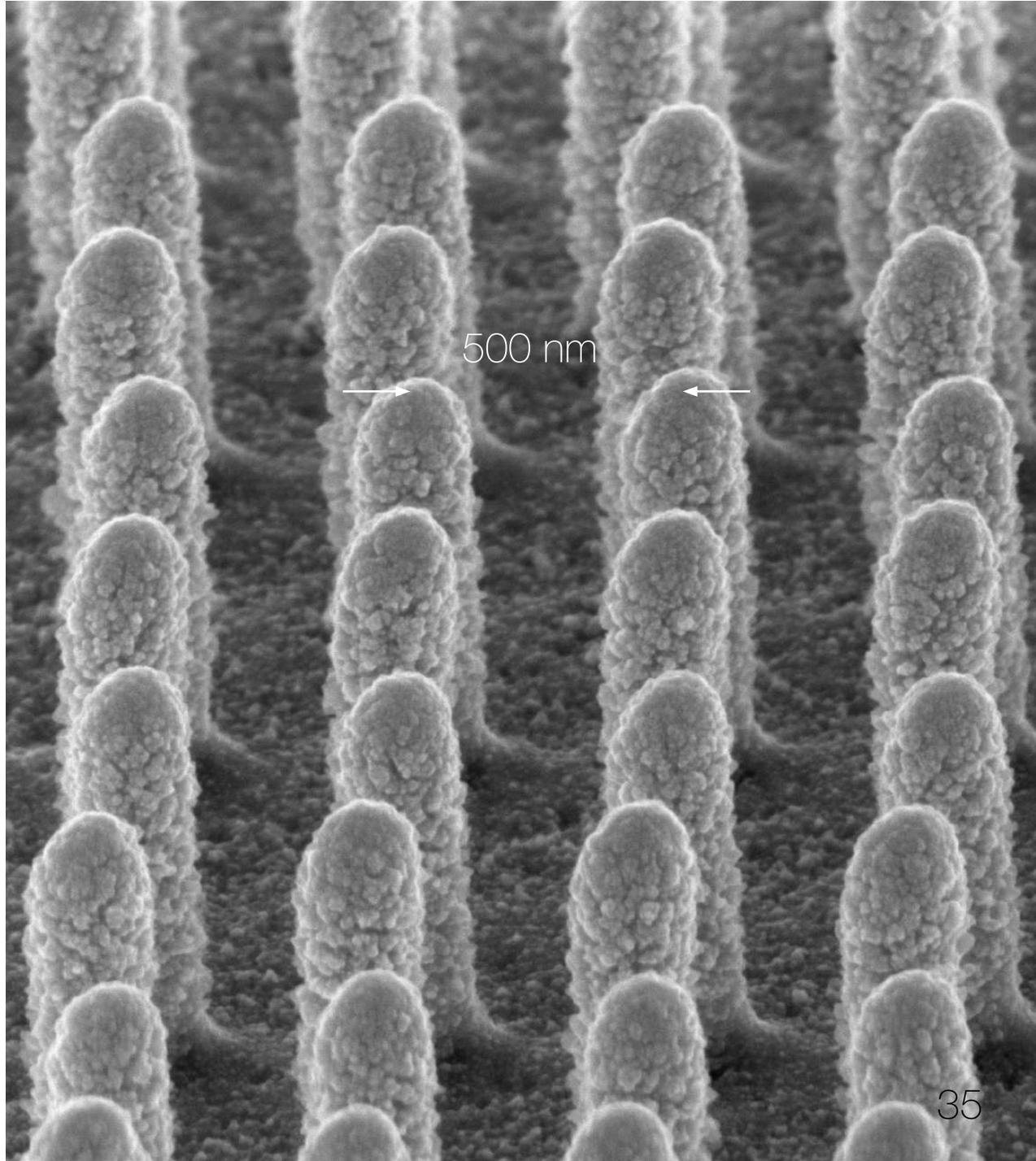
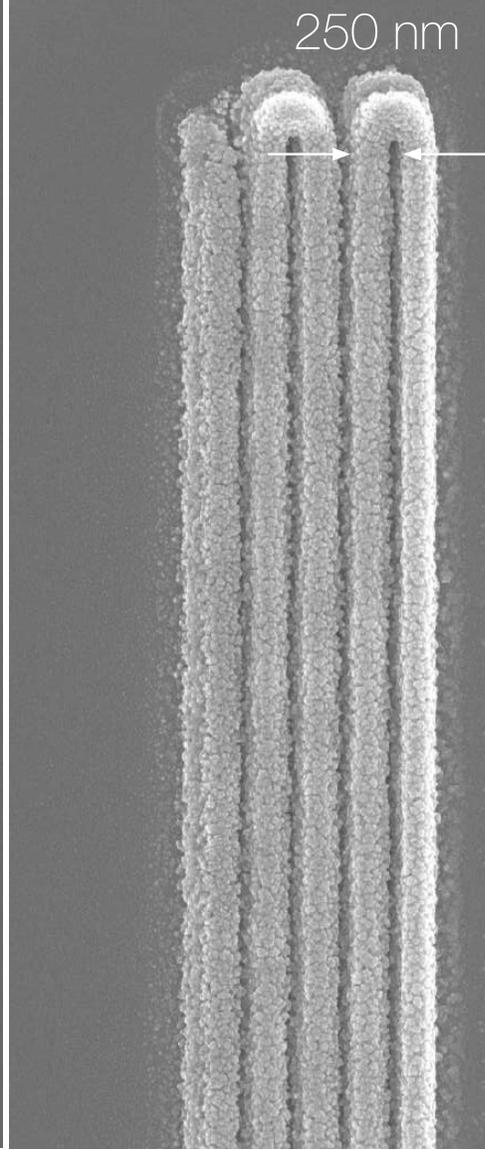
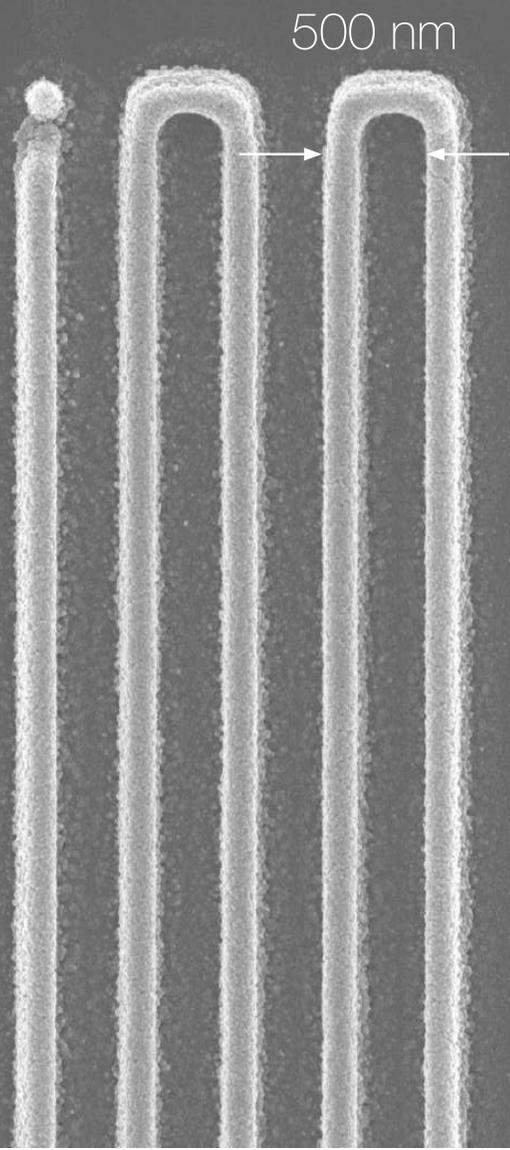
15°

$450 \mu\text{m}$

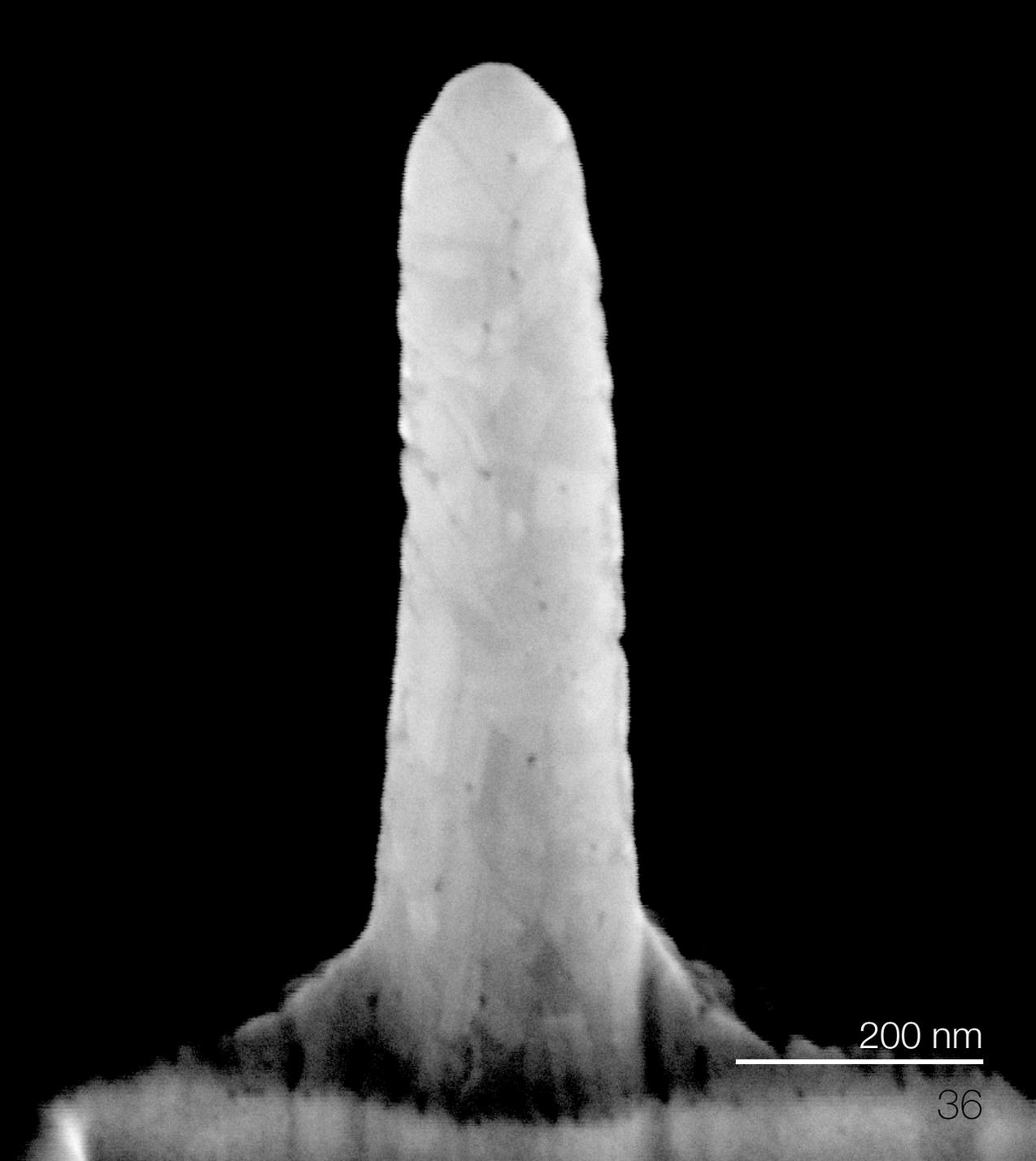
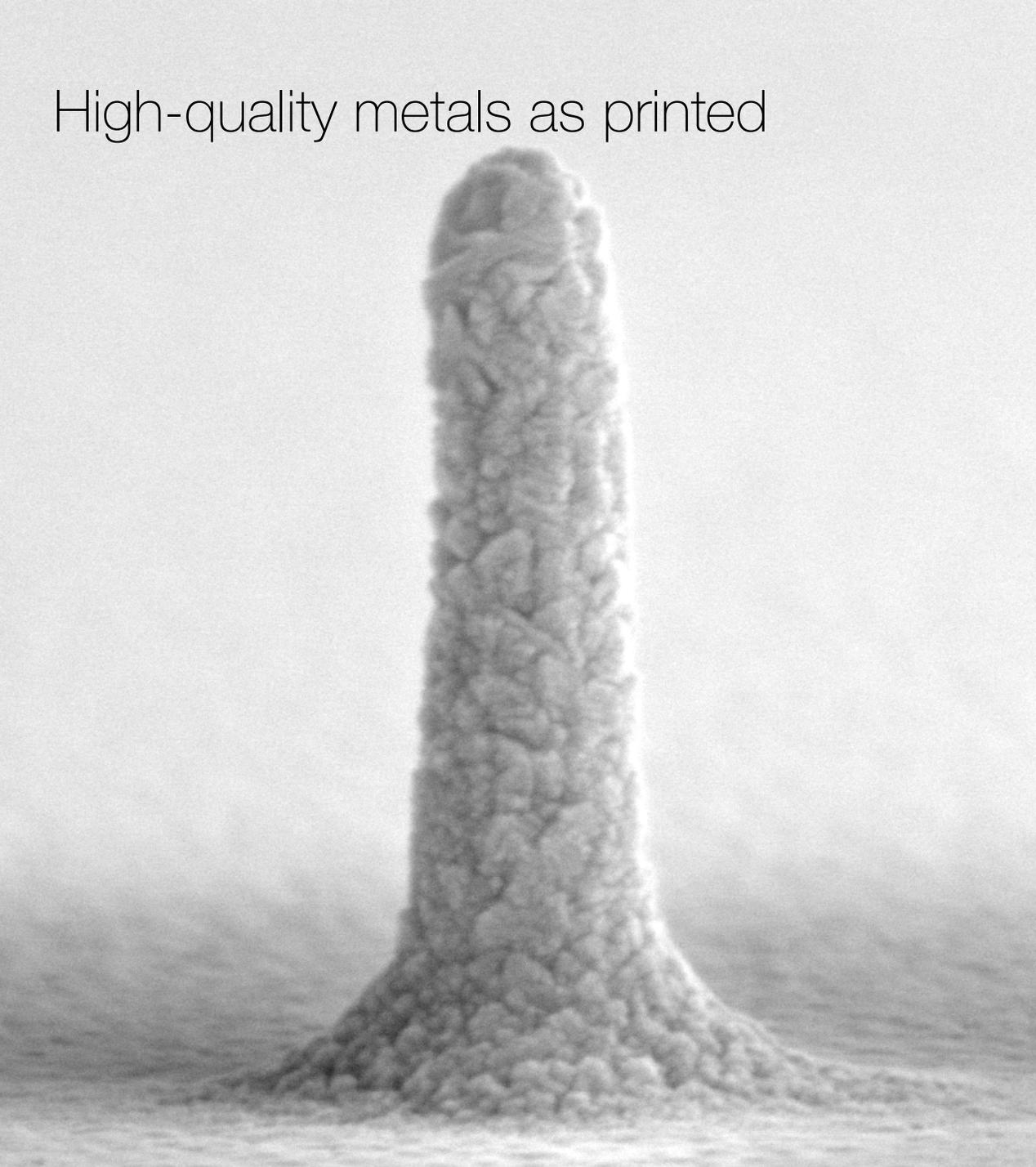
EHD-RP: one order of magnitude faster than other electrochemical methods



High resolution



High-quality metals as printed



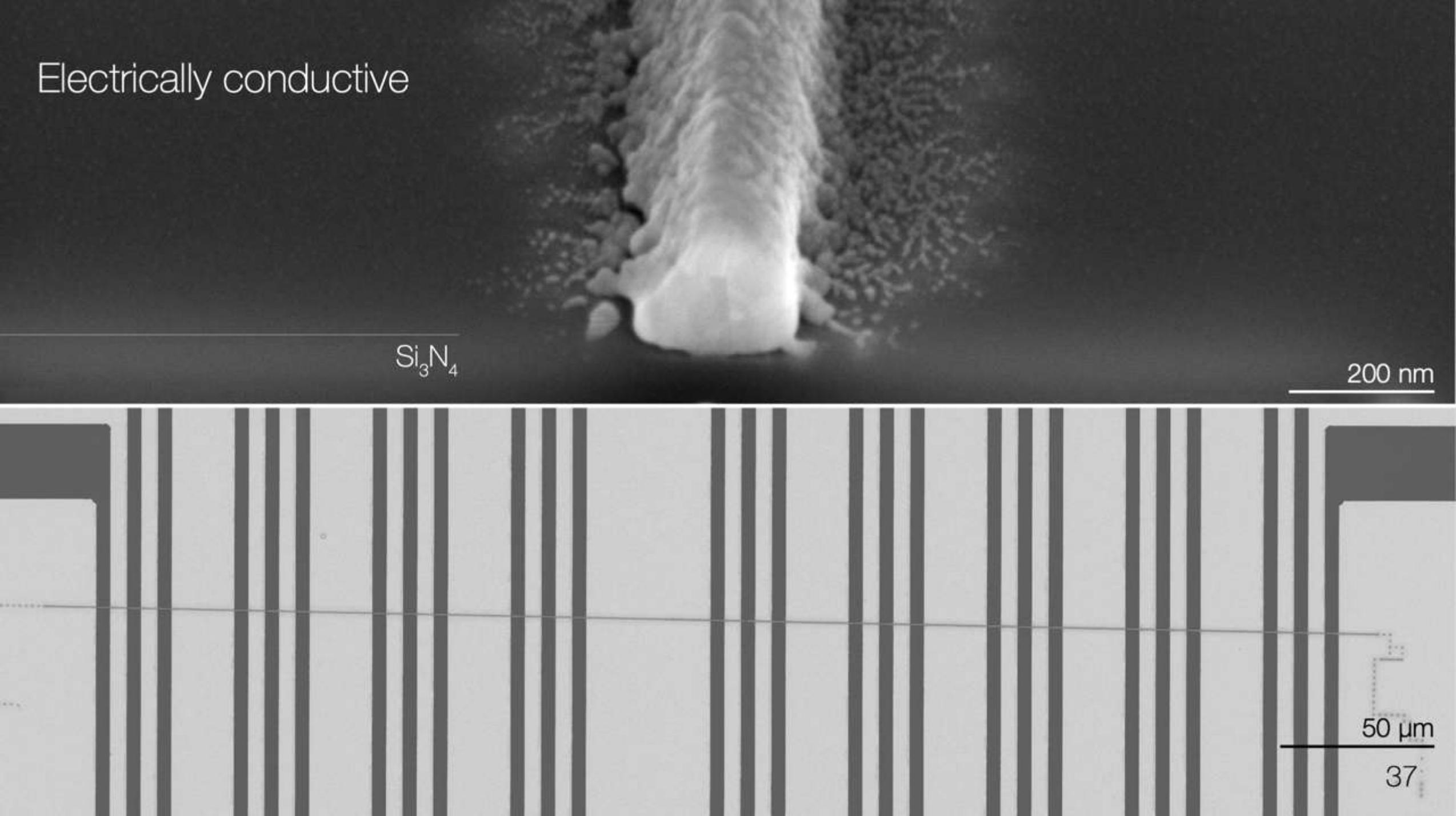
Electrically conductive



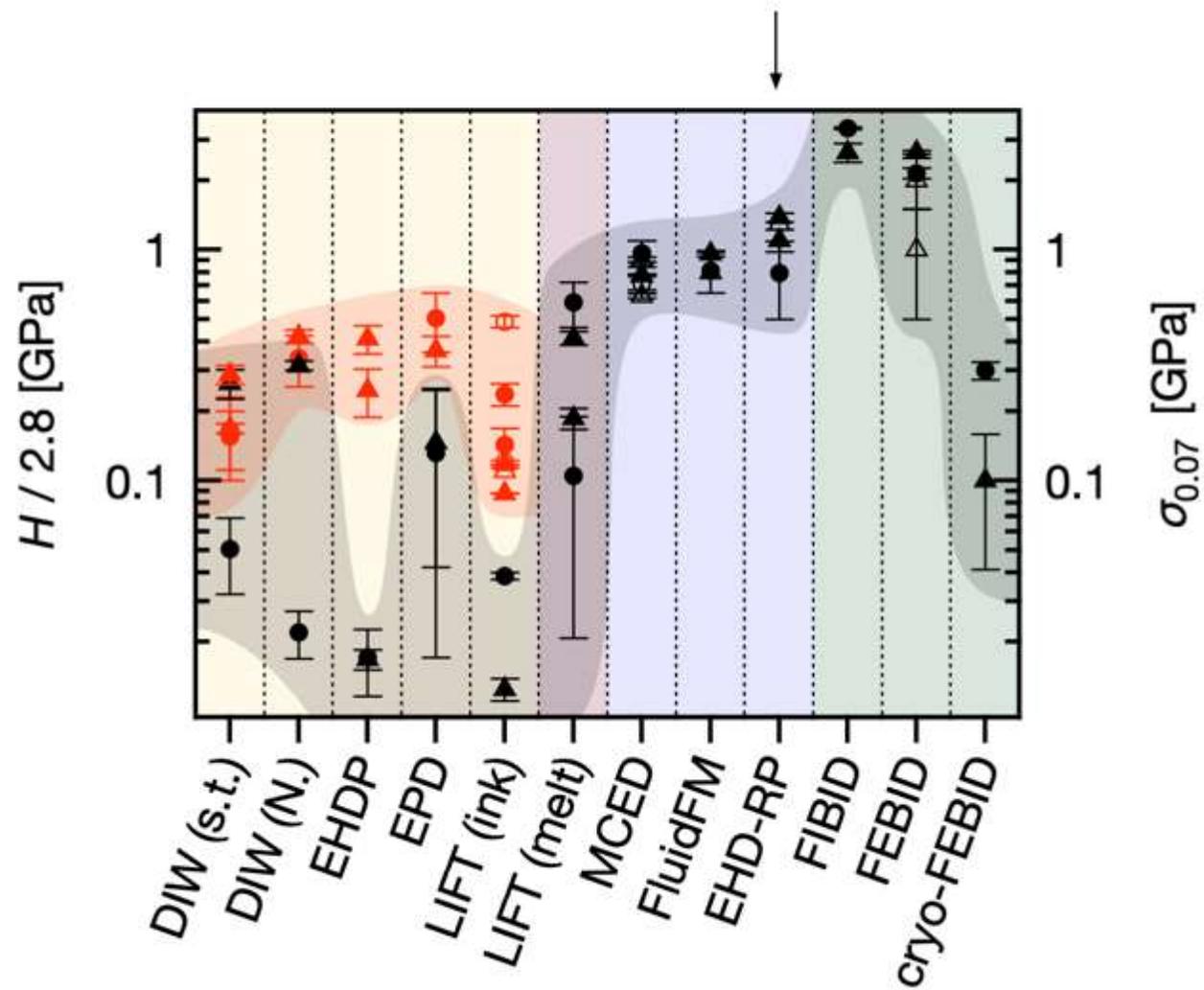
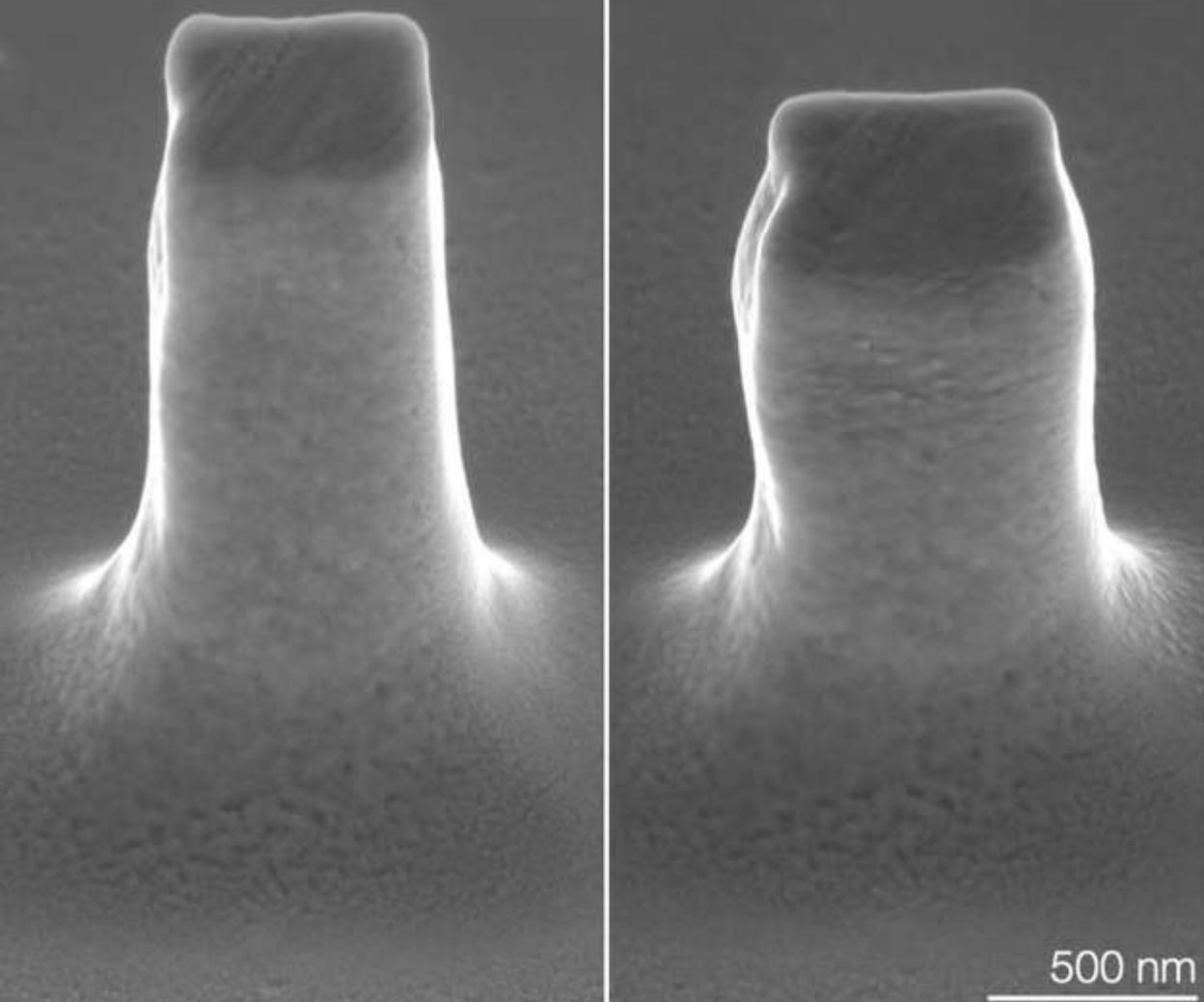
200 nm

50 μm

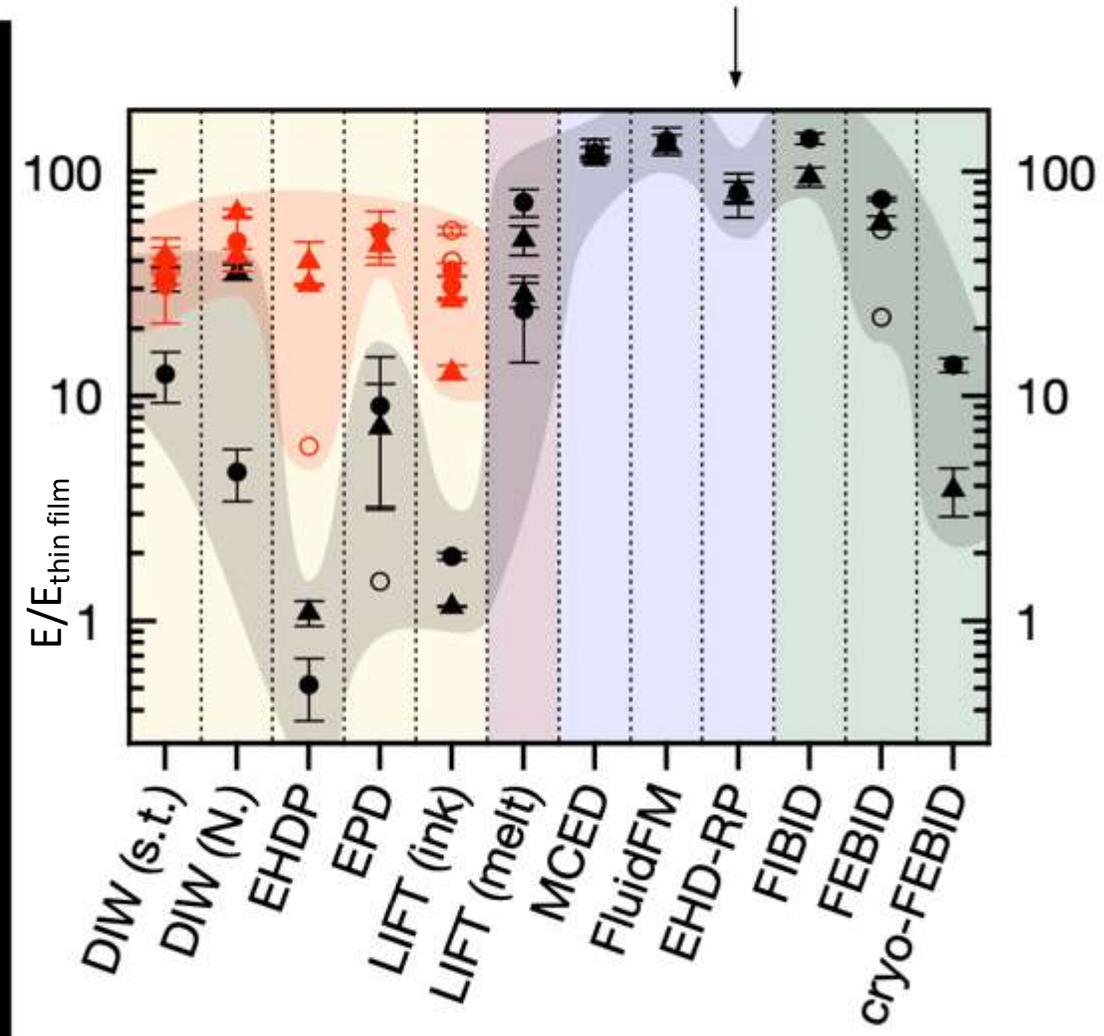
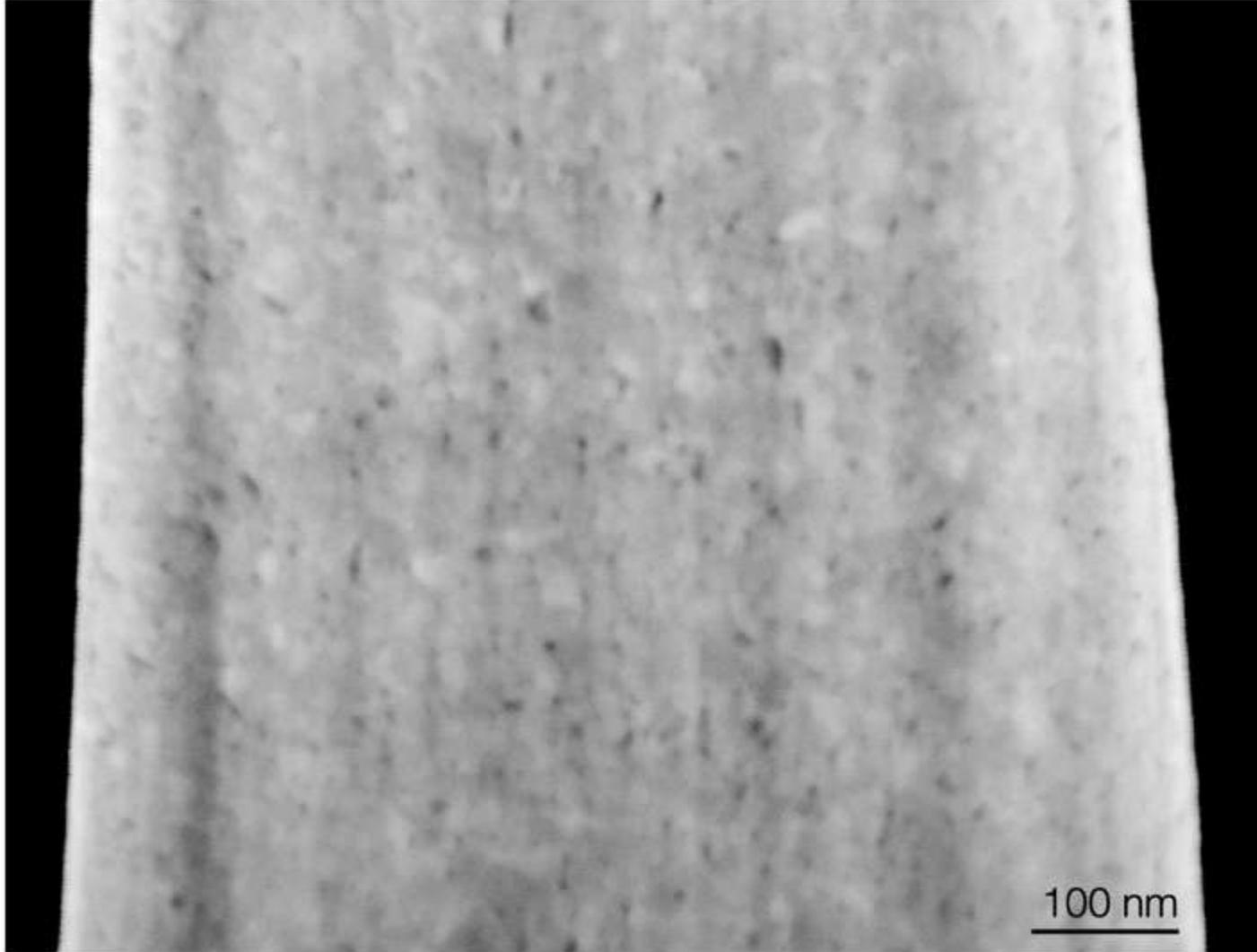
37



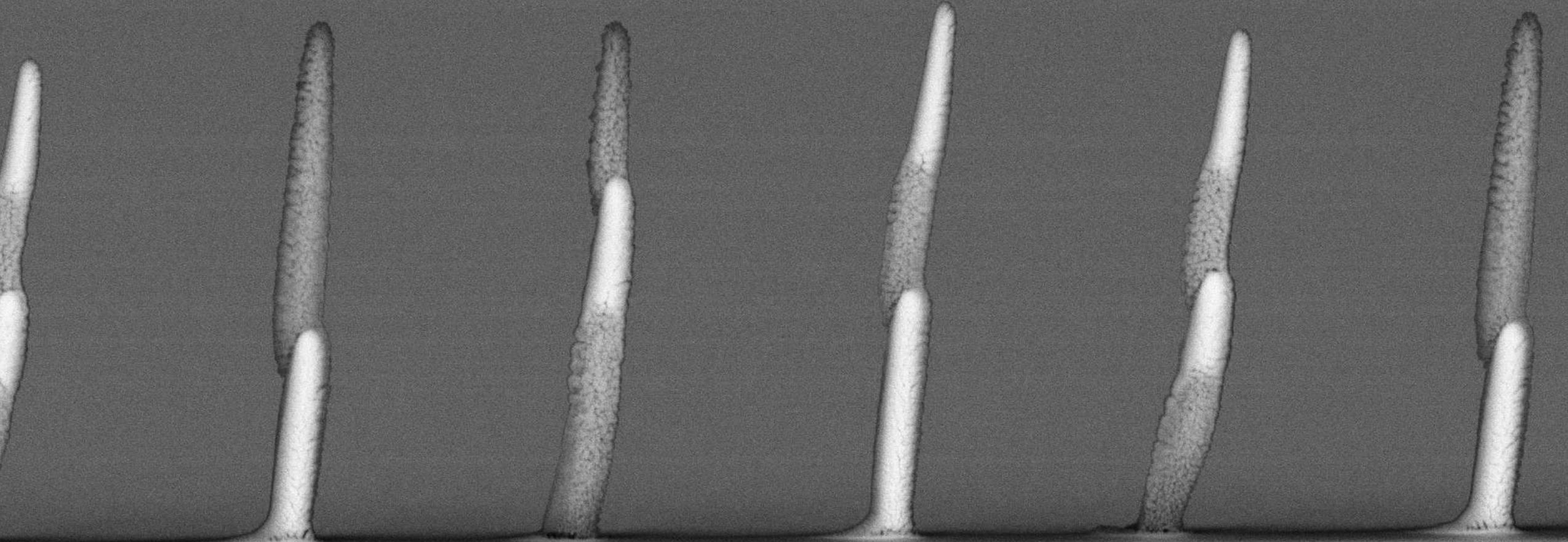
Strong



Lower modulus than bulk Cu

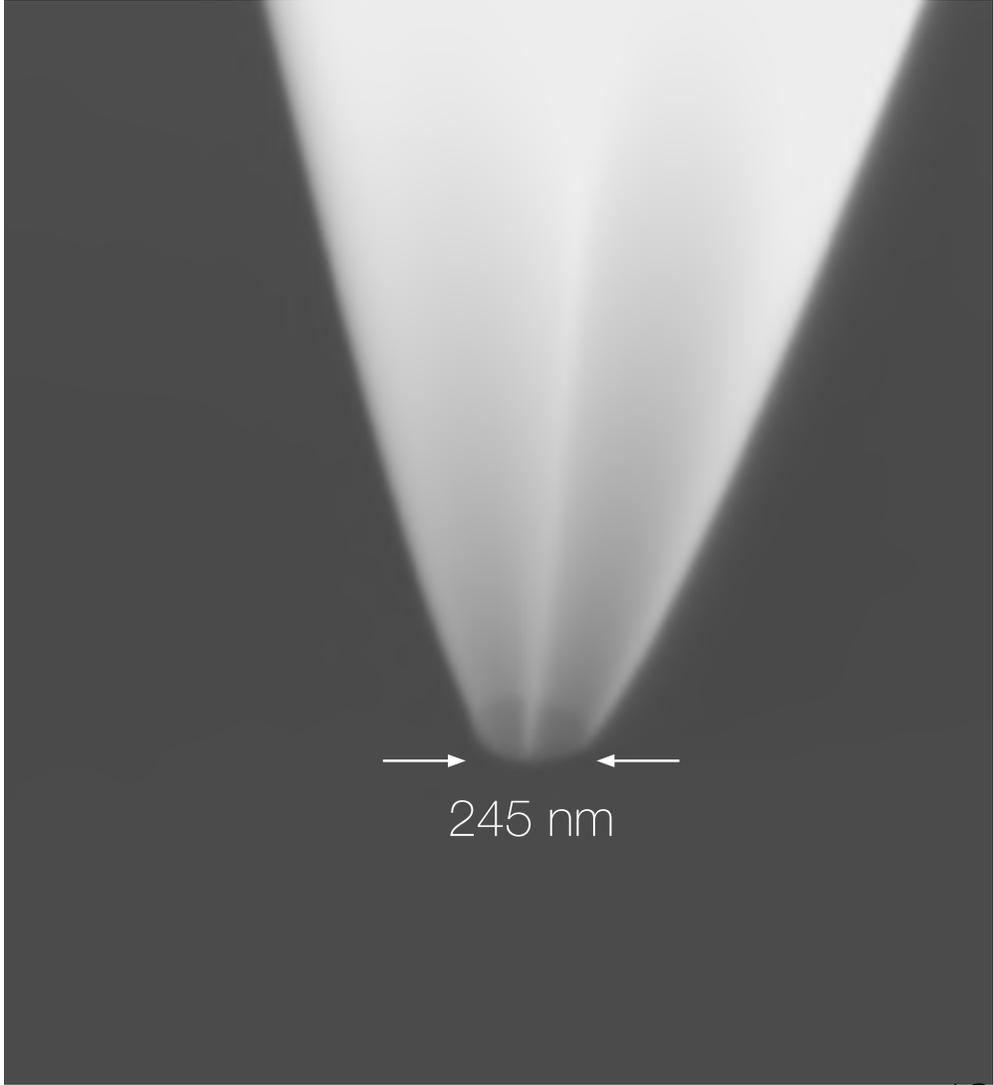
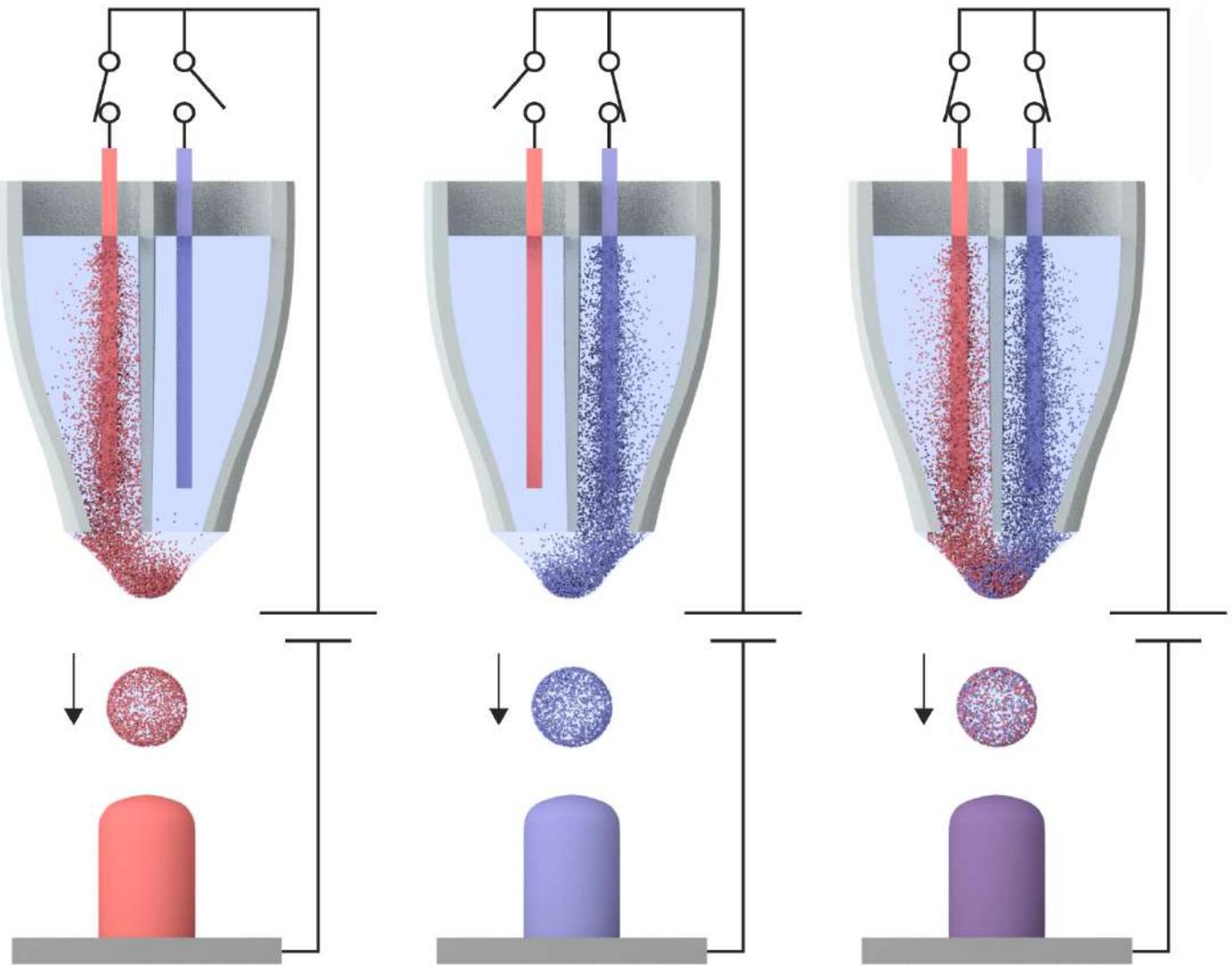


Part III: multi-metal AM by EHD-RP

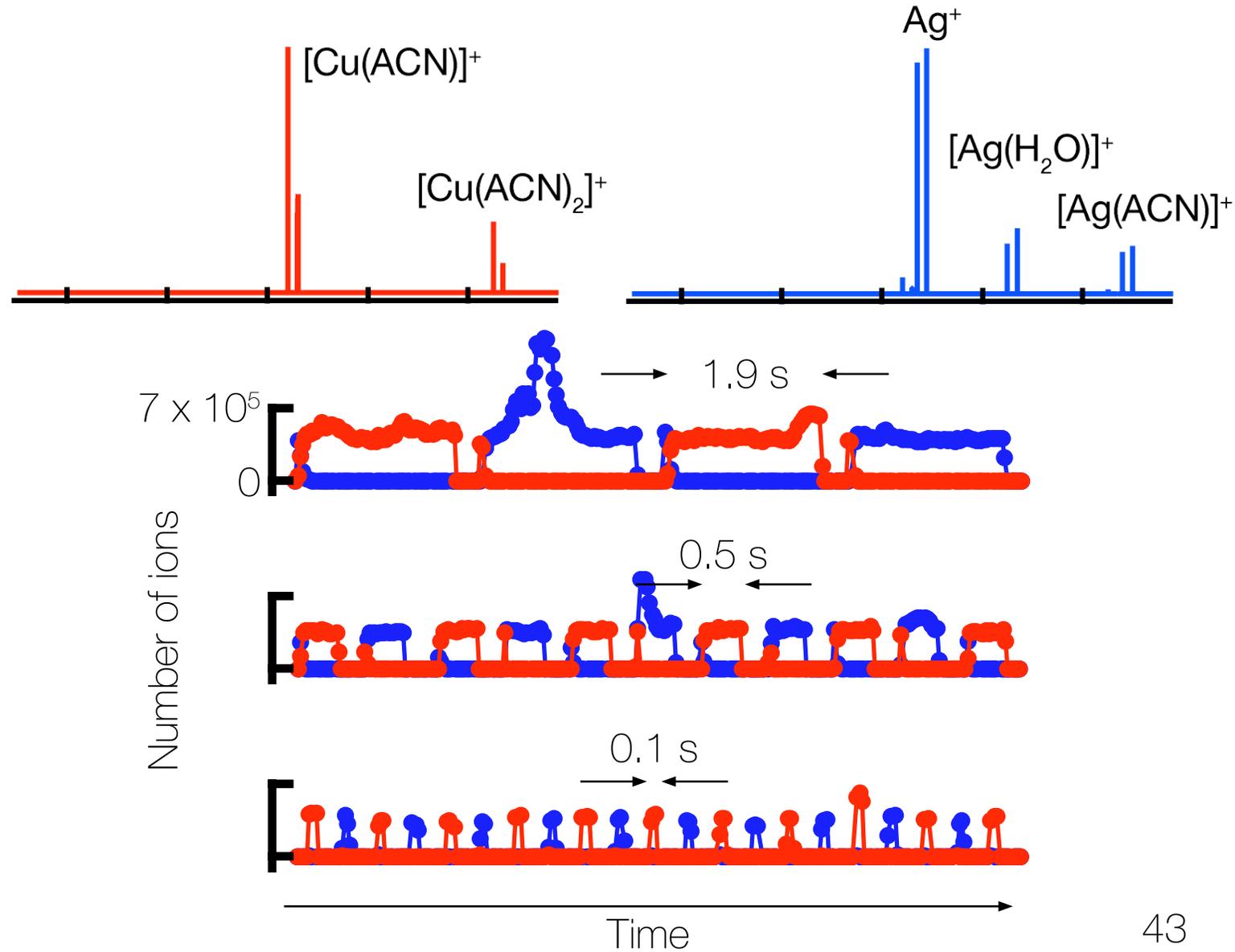
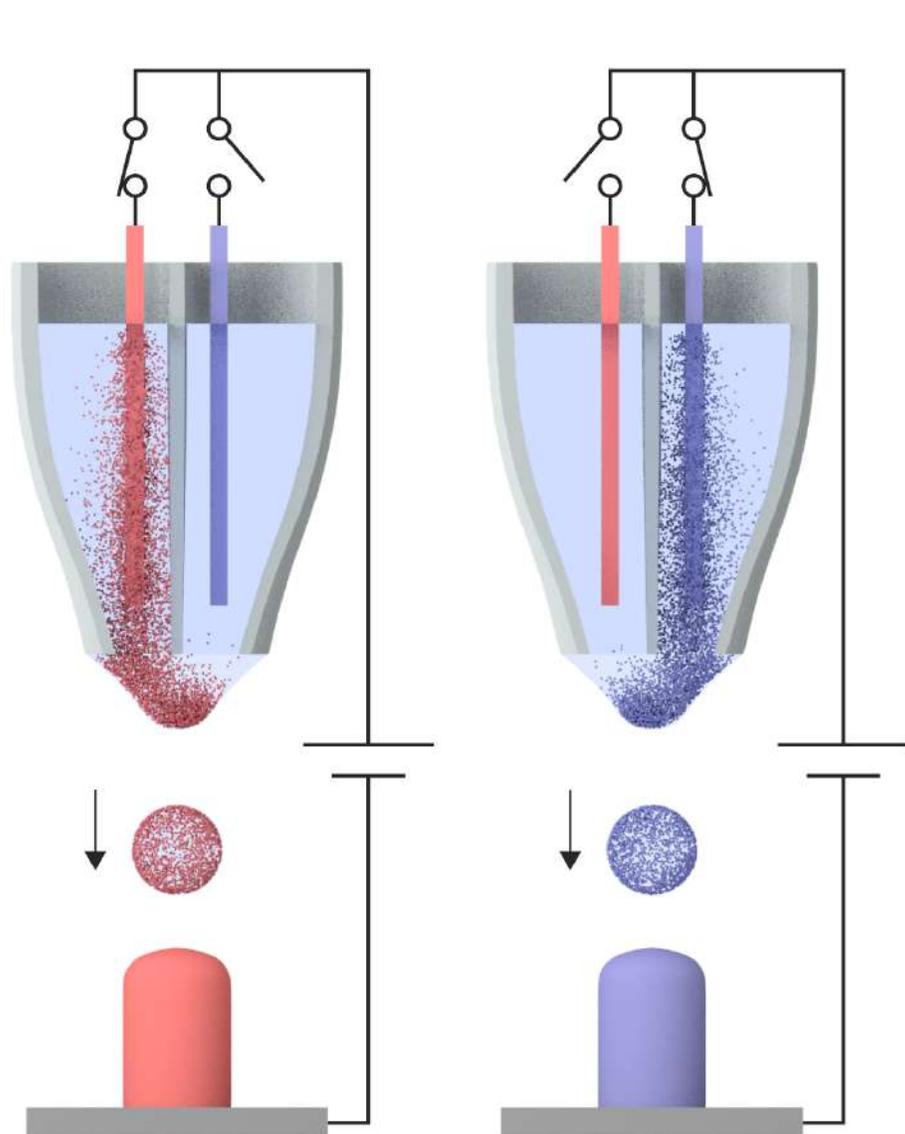


1 μ m

Multiple sources – multiple metals



In-situ generation of ions – switching on the fly



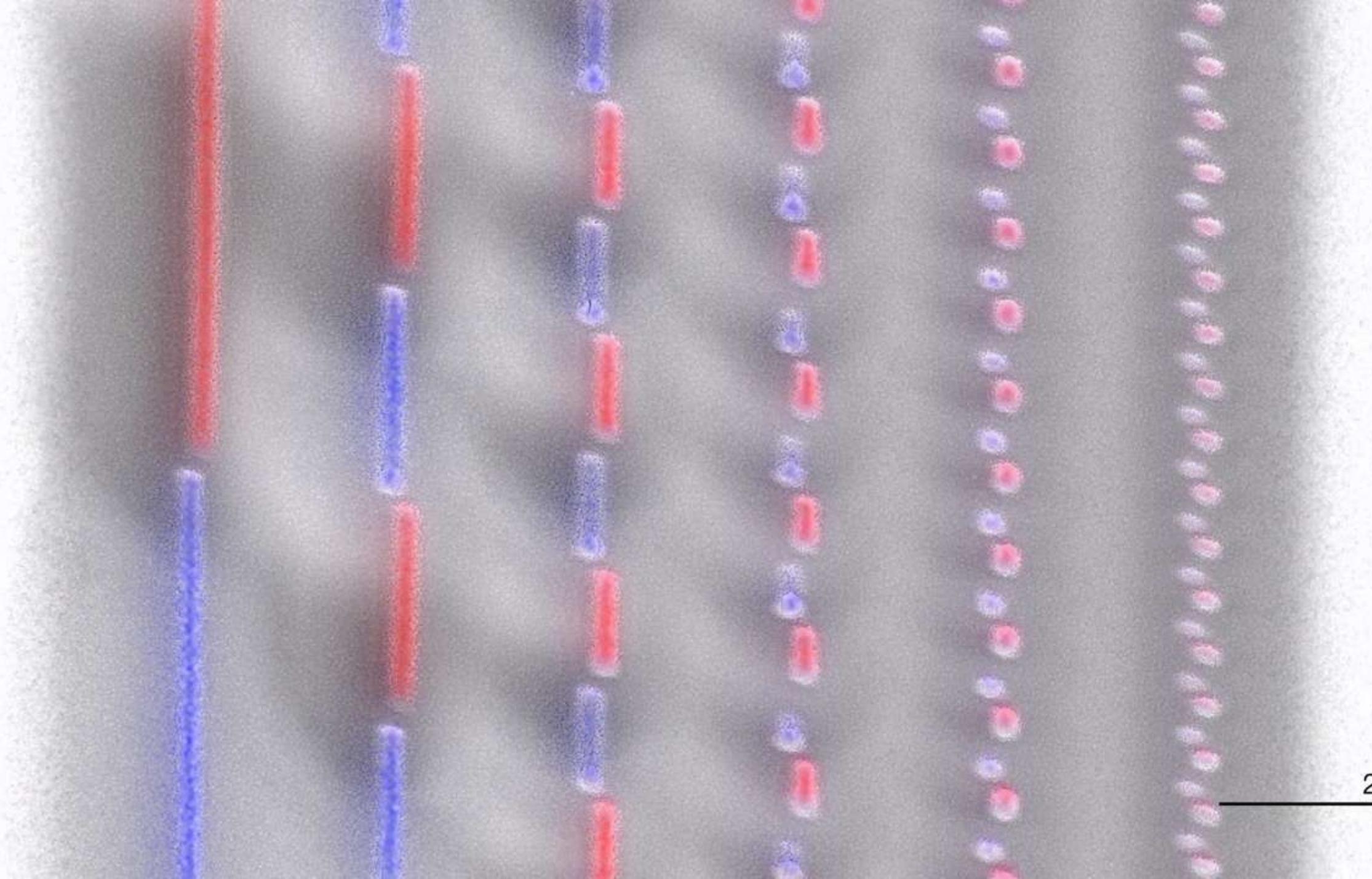
Continuous printing at $1 \mu\text{m s}^{-1}$



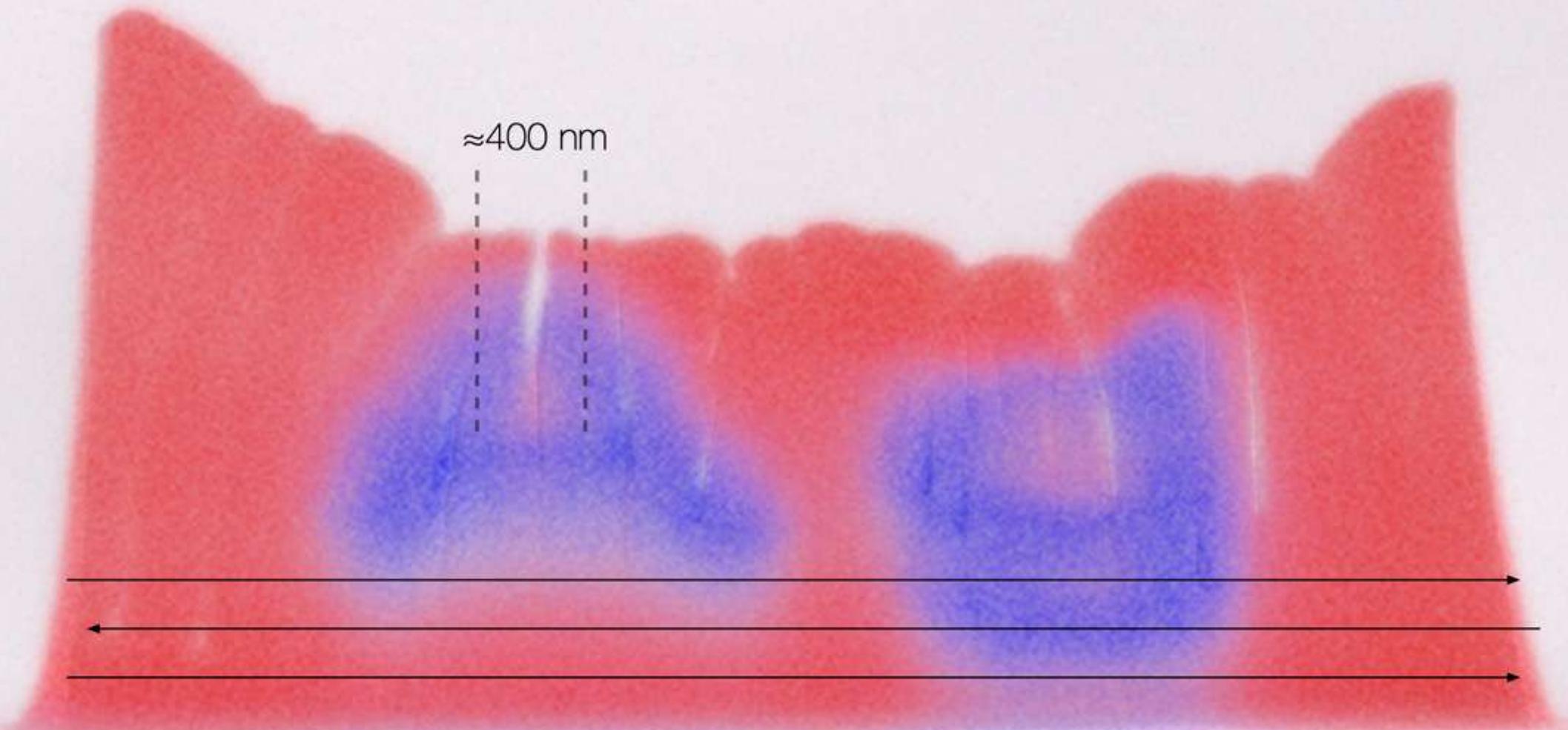
CuL
AgL

2 μm

44



Switching on the fly – complex chemical architectures



1 μm

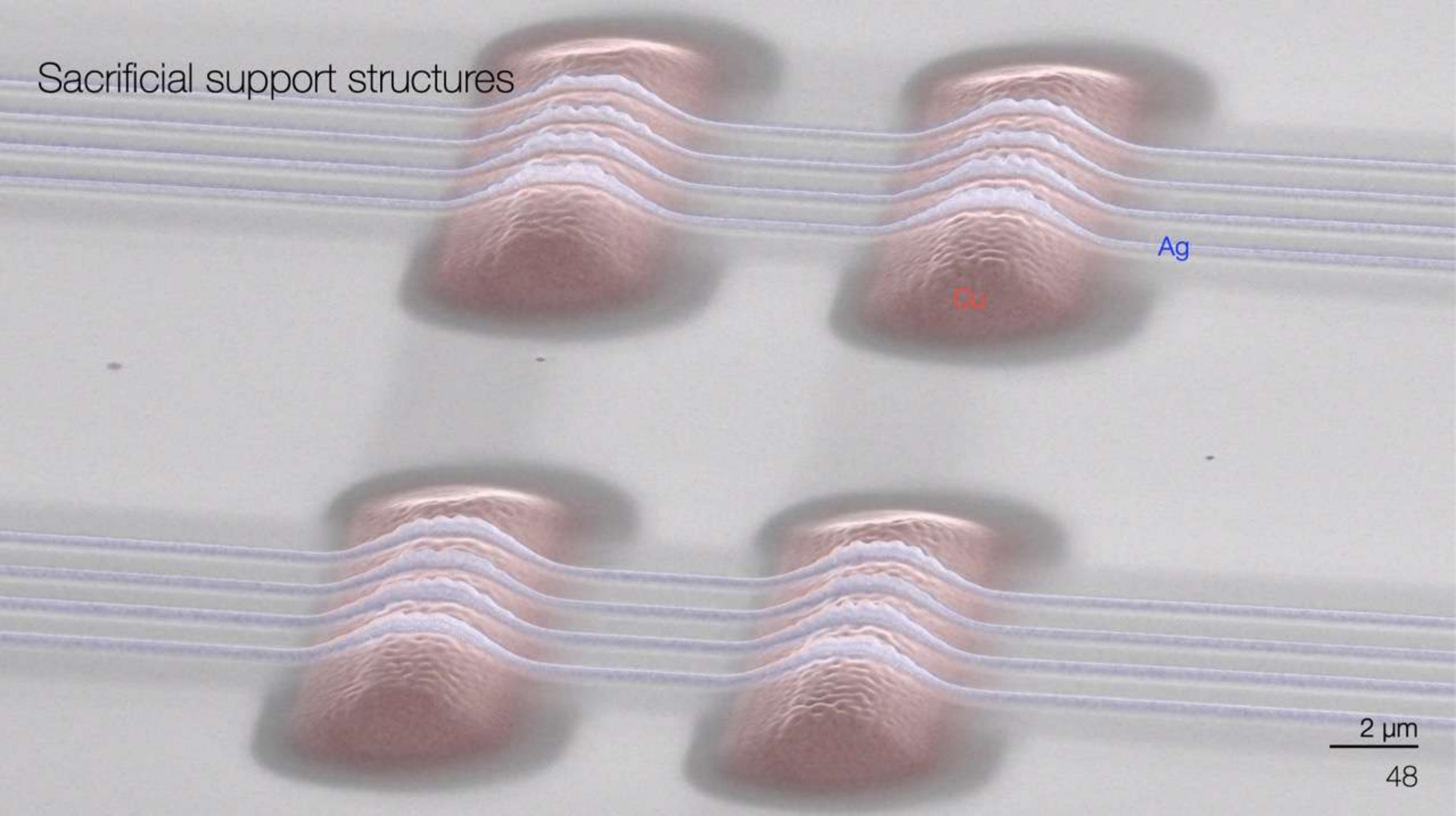
Video showing the process for printing the Ag-Cu wall from previous slide.

Please find it in the supplementary information of : *Reiser, A et al. Nature Commun. 10, 1853 (2019)*

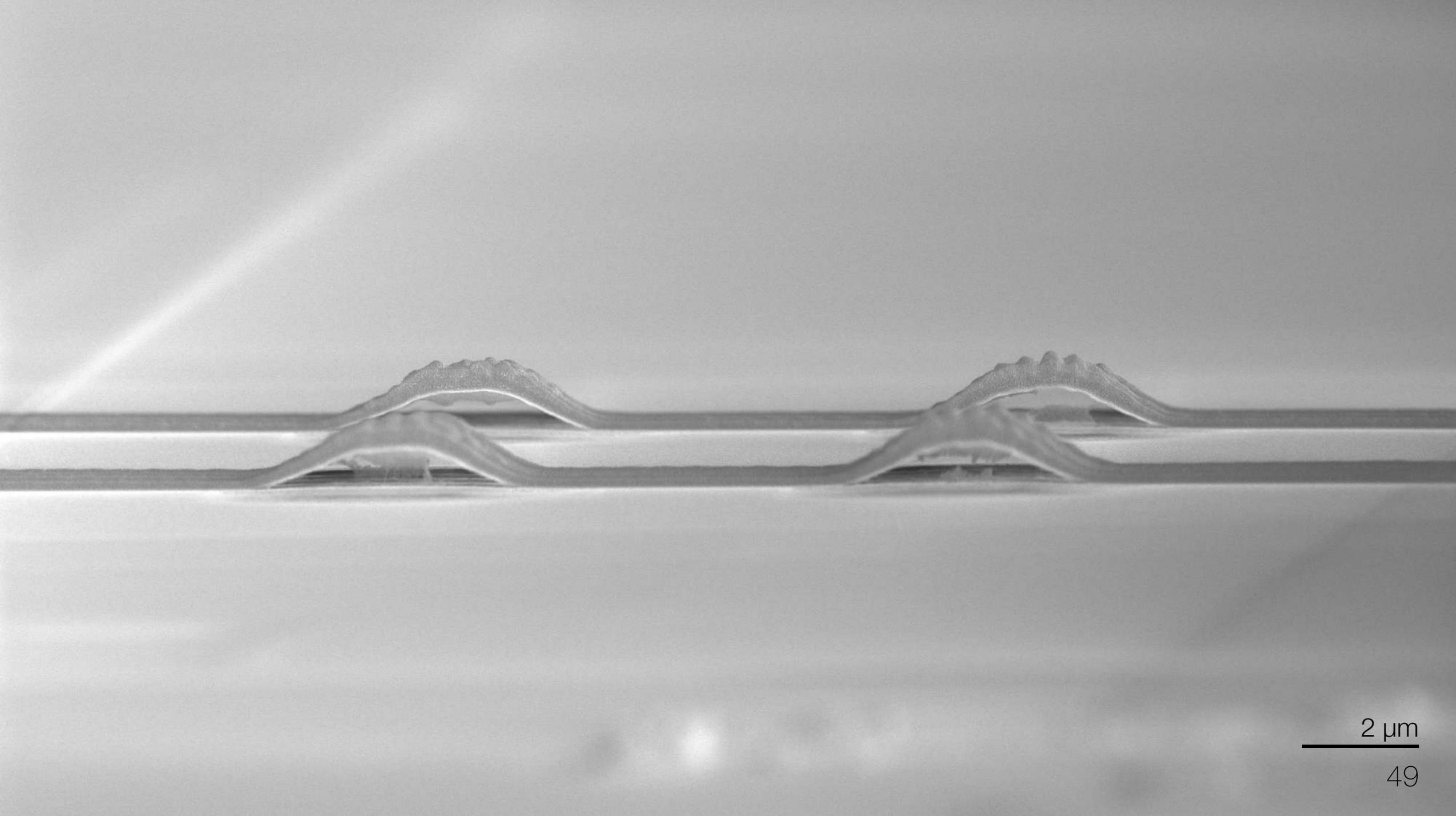
<https://www.nature.com/articles/s41467-019-09827-1#Sec13>

Supplementary Movie 1

Sacrificial support structures



2 μ m
48

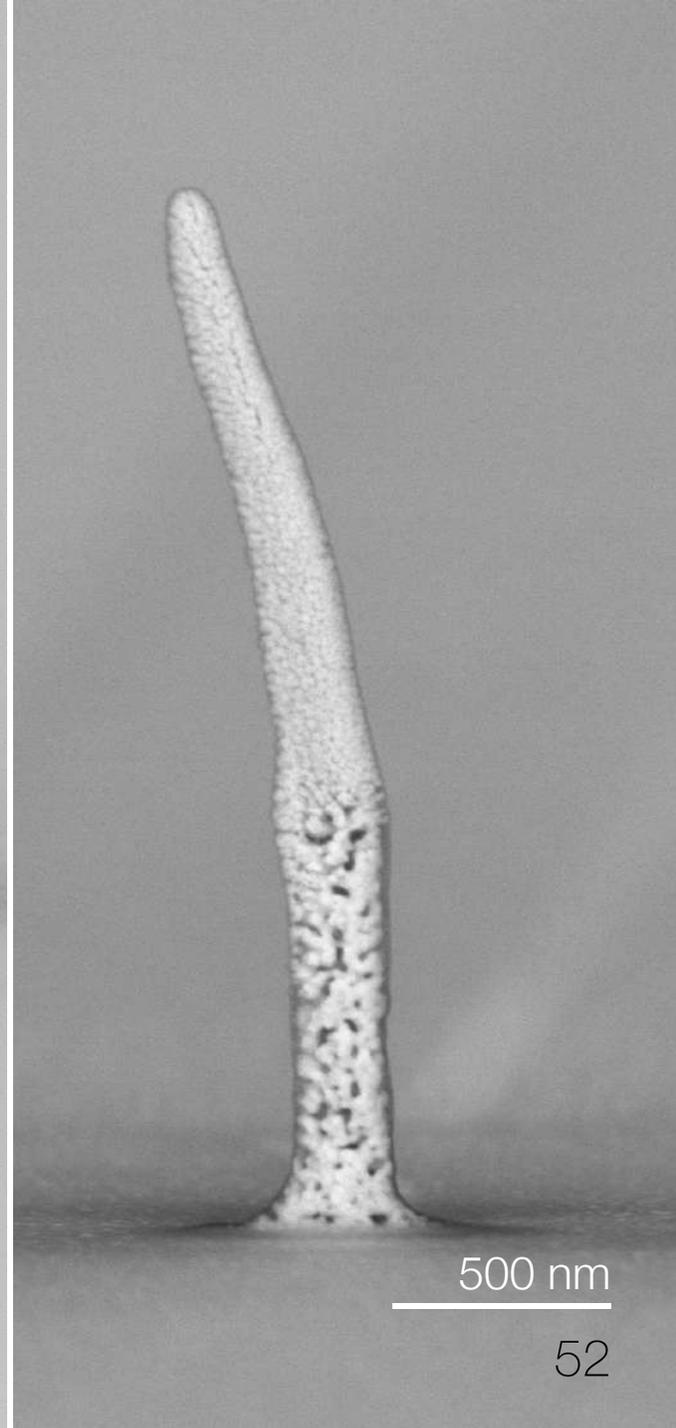
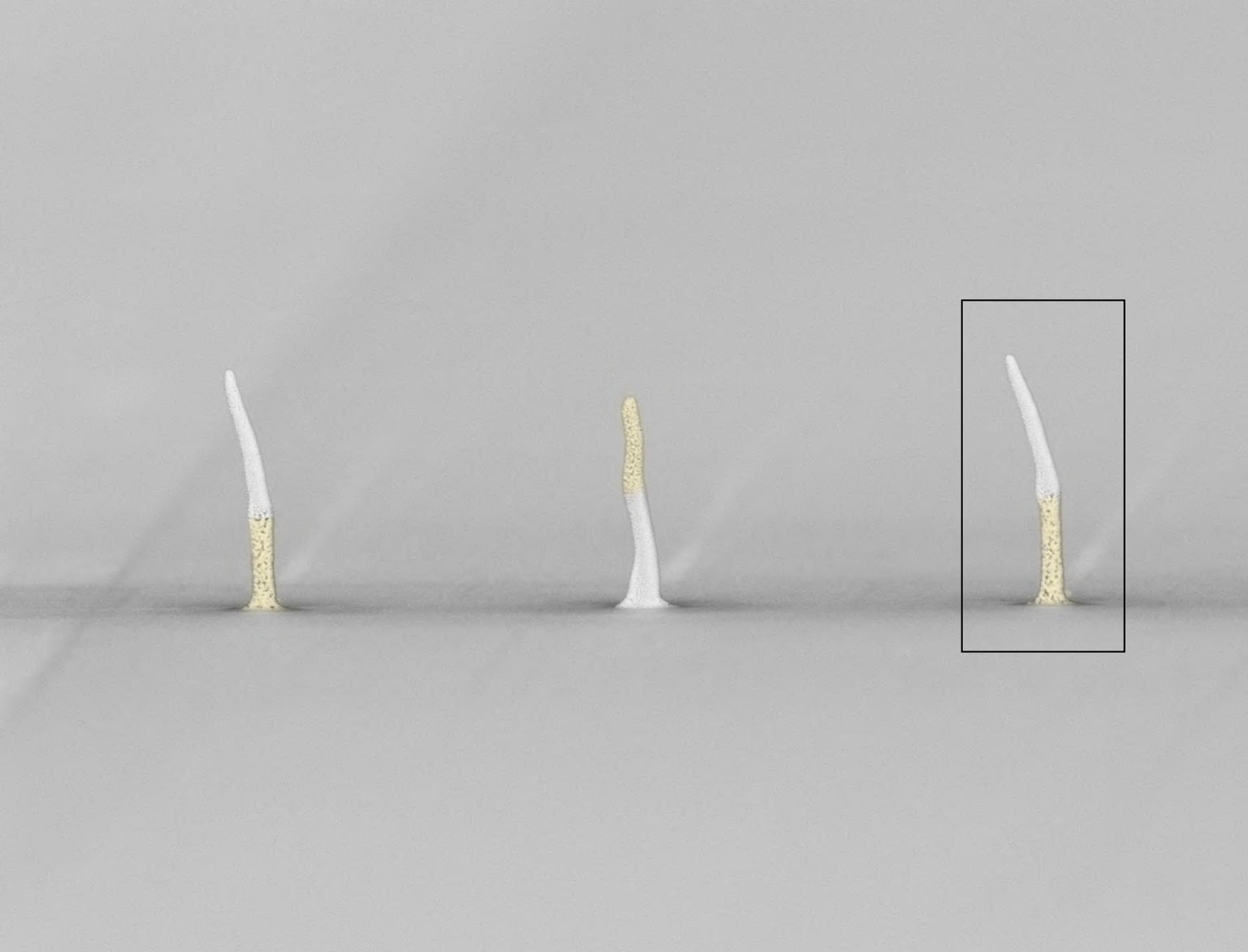


2 μm

49

Control of chemical architecture: control of local properties



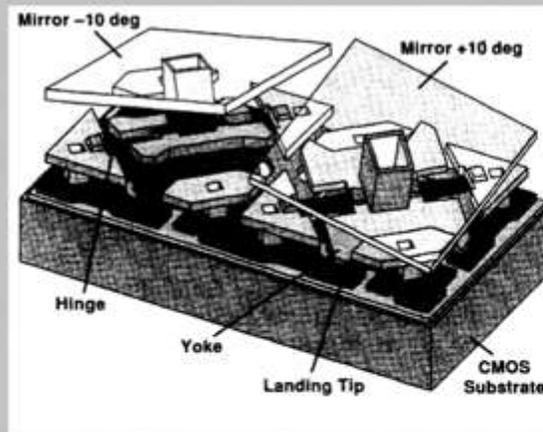


Video showing the printing process of Ag-Cu pillars and the localized plastic deformation in the nanoporous segments
Please find it in the supplementary information of : *Reiser, A et al. Nature Commun. 10, 1853 (2019)*

<https://www.nature.com/articles/s41467-019-09827-1#Sec13>
Supplementary Movie 3

sub-mircometer spatio-chemical resolution

sub-mircometer resolution high as-deposited density



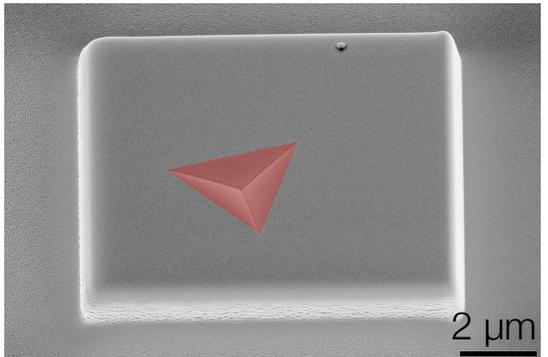
control of local alloying
and microstructure

control of local properties



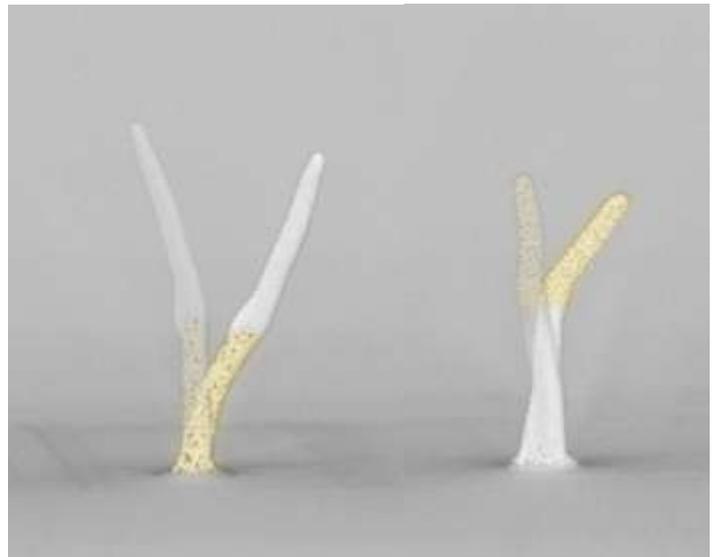
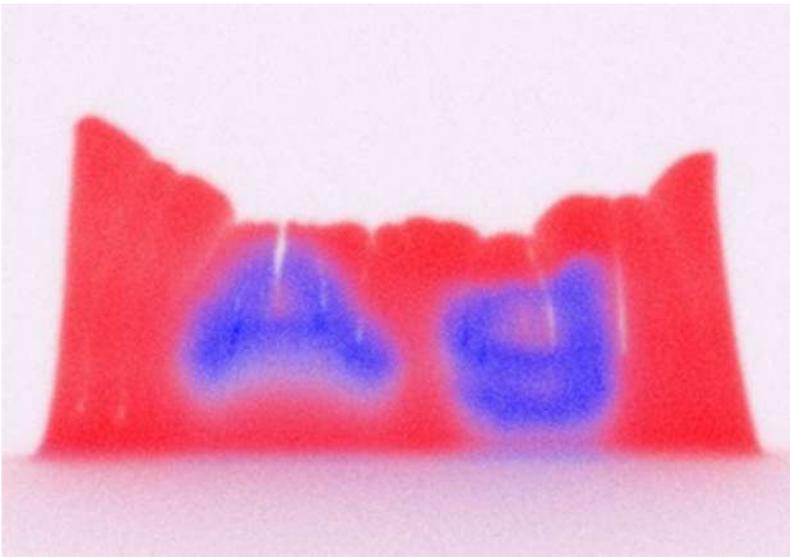
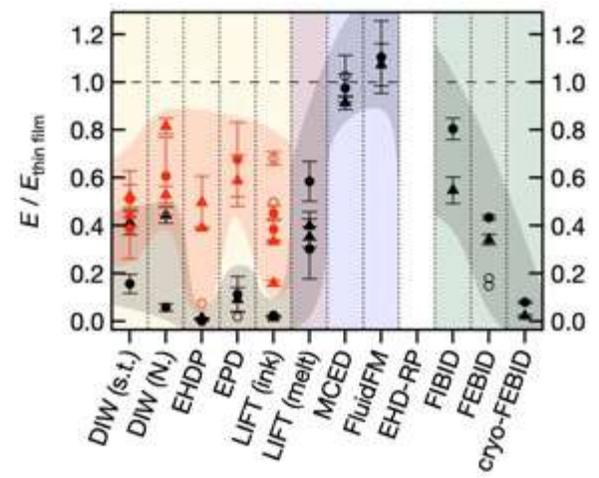
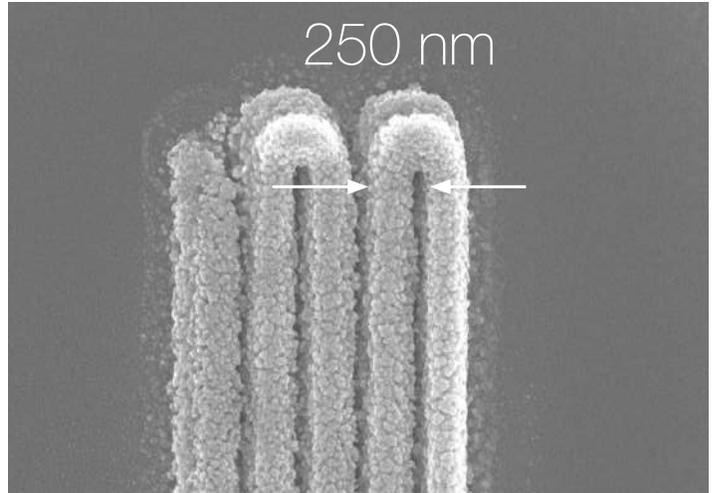
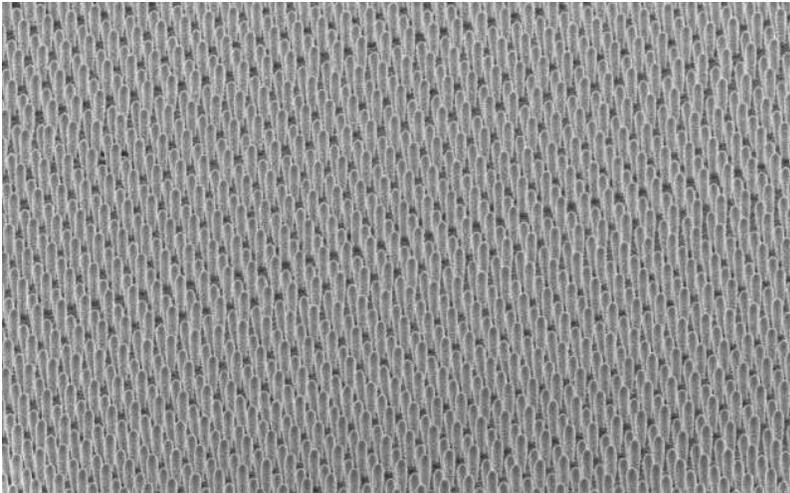
1 μ m

Microstructure and properties of printed metals



$\lambda,$

EHD-RP



1 μm

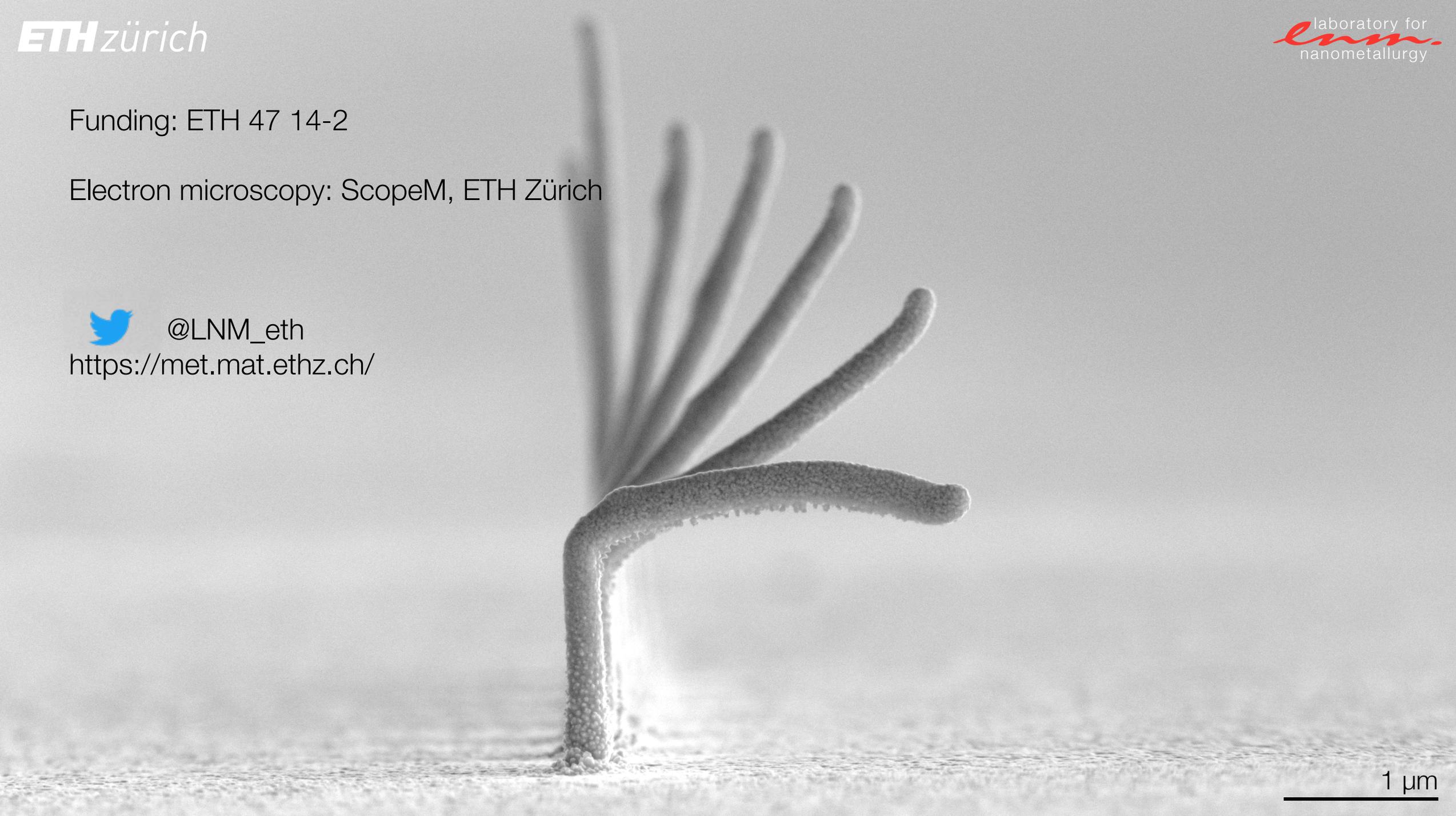
Funding: ETH 47 14-2

Electron microscopy: ScopeM, ETH Zürich



@LNM_eth

<https://met.mat.ethz.ch/>



1 μ m