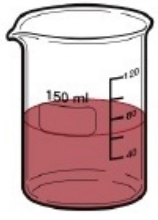
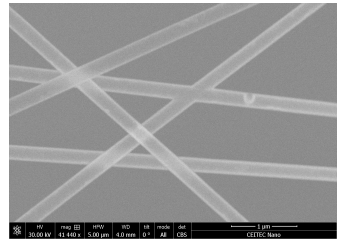
Electroless plating of magnetic nanotubes

Michal Staňo
michal.stano@ceitec.vutbr.cz



CEITEC Magnetism seminar

November 24, 2021



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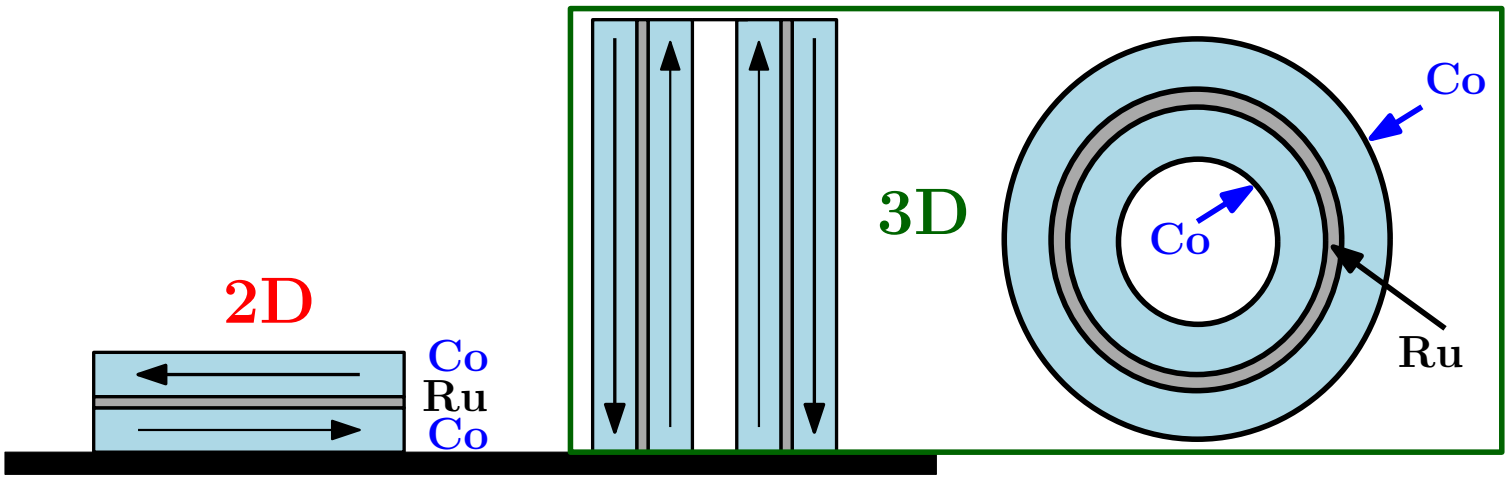
STAFF3d-spin project: http://magnetism.ceitec.cz/staff3d-spin/

STAFF3d-spin project: multilayered nanotubes

Synthesis and investigation of
Synthetic **T**ubular **A**nti**F**erromagnets **F**or **3D Spin**tronics



Overview

- Previously: Atomic Layer Deposition of Co, Ru (planar)

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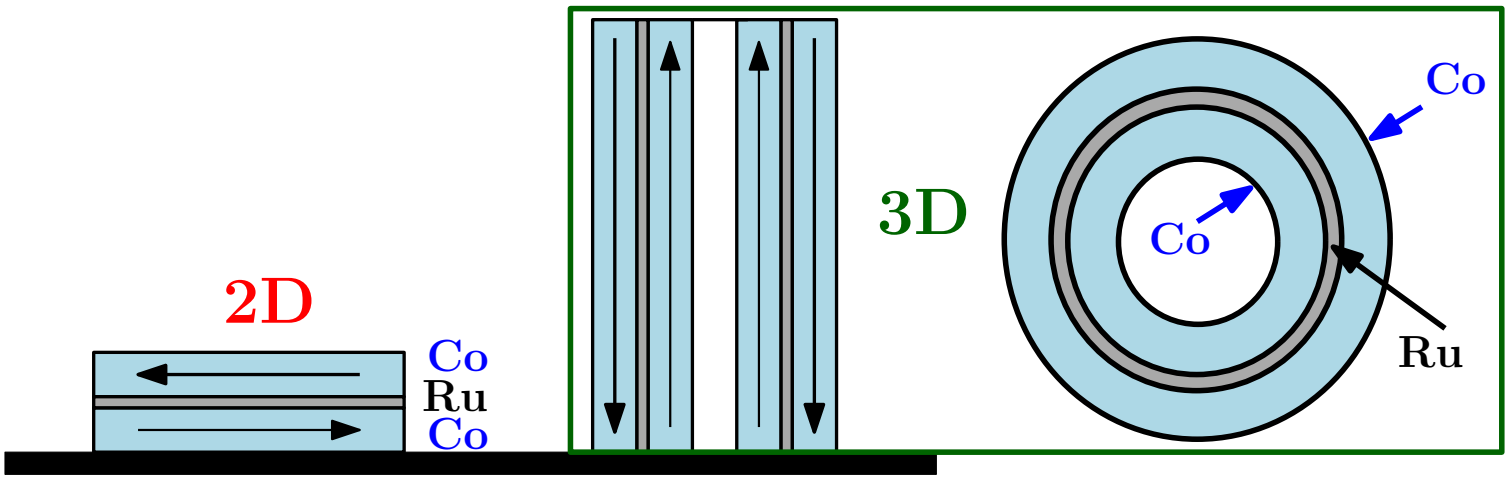


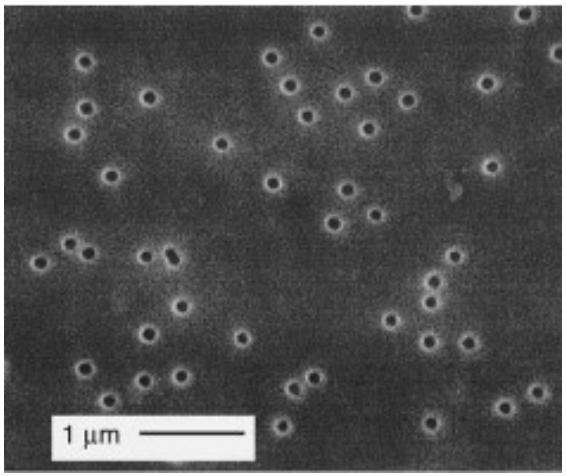
Overview

- Previously: Atomic Layer Deposition of Co, Ru (planar)
- Now: Electroless plating of magnetic nanotubes
- Now: Investigation of individual magnetic nanotubes
- Next: ? Multilayers Magnetic/Ru/Magnetic layer, further imaging, . . .

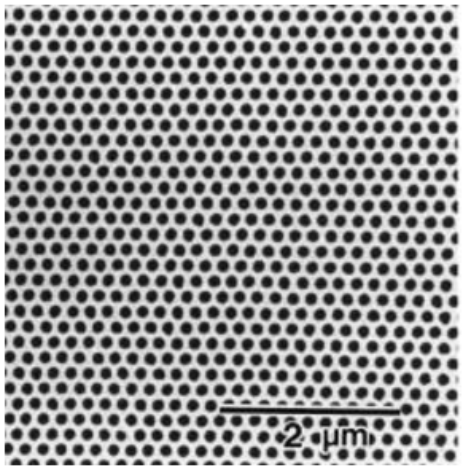
Outline of the presentation

How to prepare magnetic nanotubes?

For small uniform diameters and large scale production:
bottom-up approach + a **template** (porous membrane)



Ion-track-etched polycarbonate



Nanoporous anodized alumina

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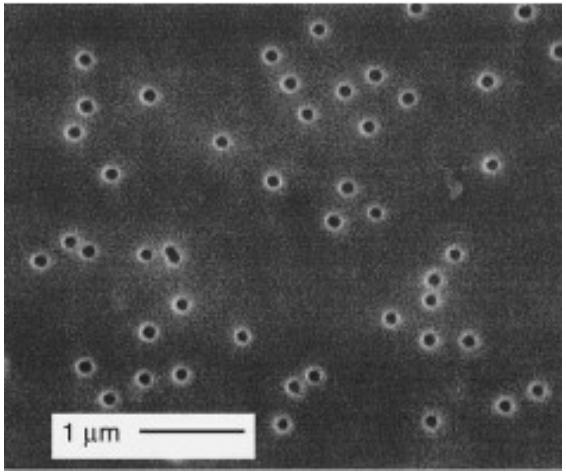

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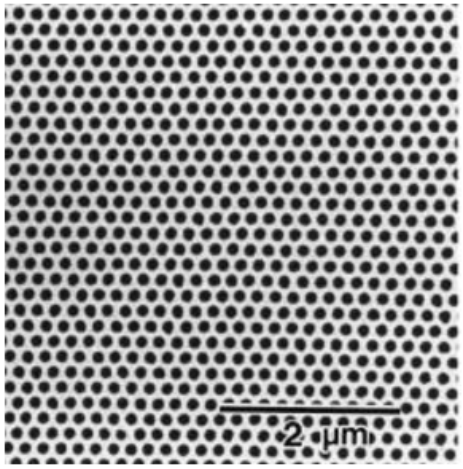

Nanoporous anodized alumina

- Atomic layer deposition
- **Electroless deposition**
- Electrochemical deposition (electroplating)

Other deposition methods: Sol-gel, thermal decomposition, ...

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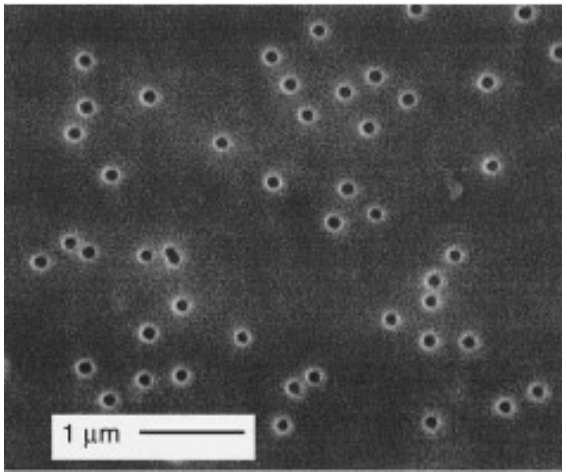

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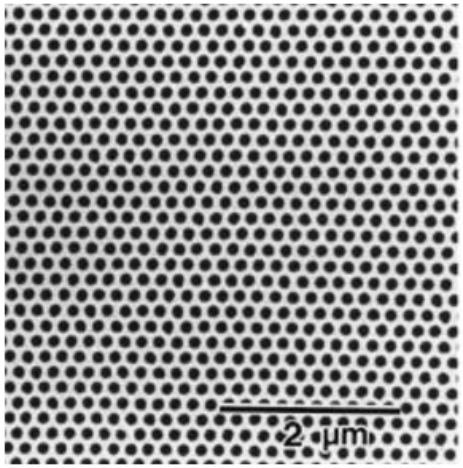

Nanoporous anodized alumina

- Atomic layer deposition
- **Electroless deposition**
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Other deposition methods: Sol-gel, thermal decomposition, ...

Alternative: coating of vertical nanopillars with chemical or physical deposition

Electroless plating – What can be achieved?

Examples from the literature:

U Limerick, Prof. Rhen:

- NiFeB, CoB, NiCuB, CoNiFeB [*Phys. Procedia* **75**, 1158-1166 (2015)]

TU Darmstadt, Prof. Ensinger:

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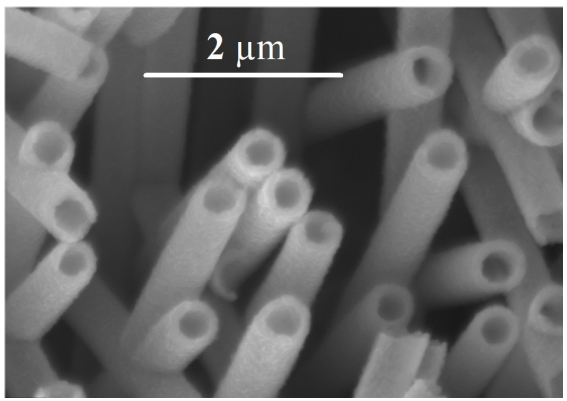
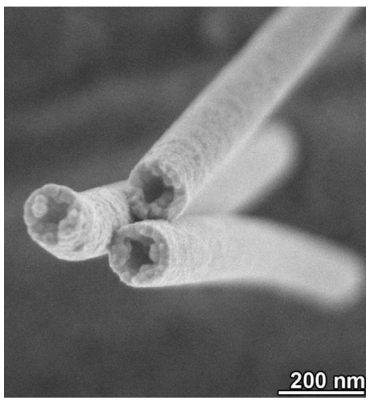


NiFeB [U Limerick]



Au [TU Darmstadt]

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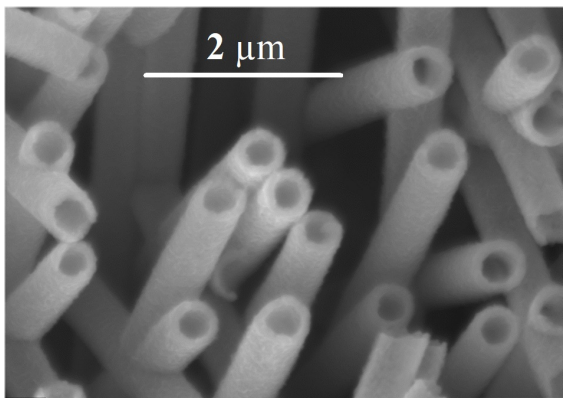

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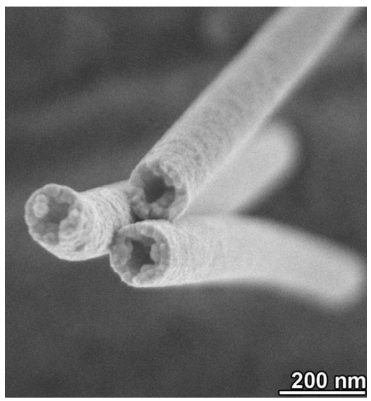

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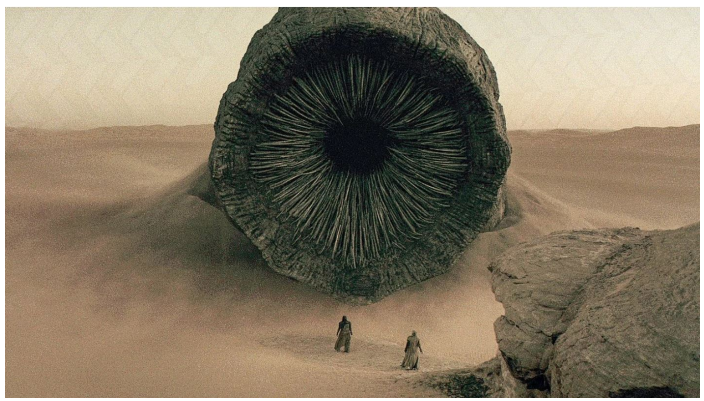

'tube' from Arrakis [Dune 2021]

Electroless plating – How it works

Autocatalytic deposition: catalyzed reduction of metallic ions
$M^{n+} + ne^- \rightarrow M^0$ (s)

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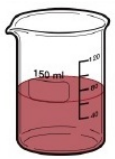

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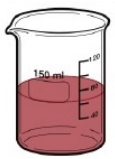

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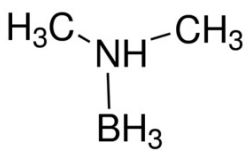

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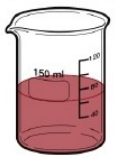

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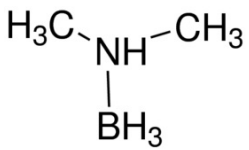

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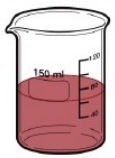

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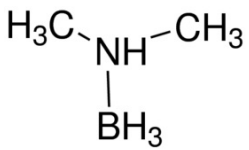

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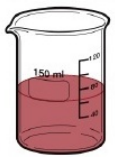

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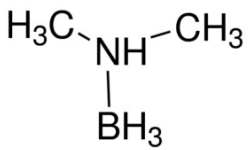

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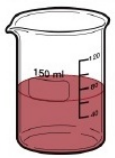

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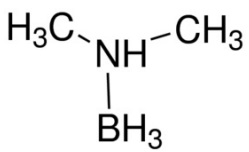

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Additional element in the deposit: B, P, N (from the reducing agent)

Electroless plating: ±, industrial applications

- \+ conformal uniform coating (uneven surfaces, complex shapes)
- \+ low cost (simple 'beaker chemistry')
- \+ low processing temperature (room temperature or $< 100\,^{\circ}\mathrm{C}$)
- * variety of materials, variety of substrates (inc. non-conductive)
- * growth rate spanning 1-100 nm/min (up to 10^1 microns/h)
- \- less precise thickness control (compared to ALD)
- \- challenge: getting continuous < 10 nm metallic layers
- \- plating solution – limited lifetime, complex composition

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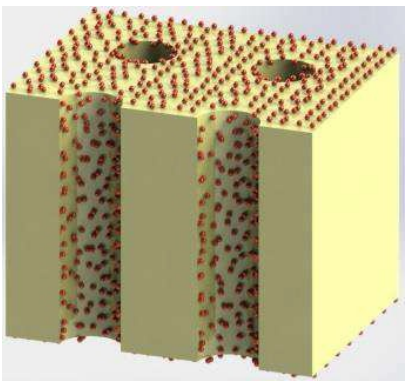
http://www.silchrome.co.uk/

- **Industry**: automotive, oil & chemistry, electronics, aerospace, . . .
- **corrosion and wear protection**, conductive paths (seed layers), shielding
- electroless **Ni-P**, Cu, composites

Electroless deposition of nanotubes

Conformal coating of modified walls of porous template

- Surface sensitization ($SnCl_2$), activation with Pd seeds ($PdCl_2$)
- Selective deposition (metal reduction) on Pd seeds (plating bath)



Template with Pd seeds

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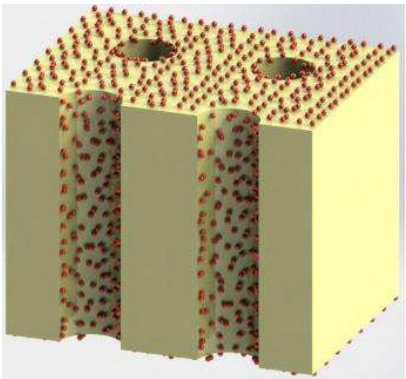

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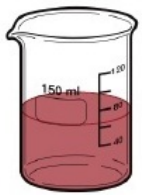

Plating bath

metal salts ($CoSO_4$, $NiSO_4$)
reducing agent (DMAB)
stabilizing agent (sodium citrate)

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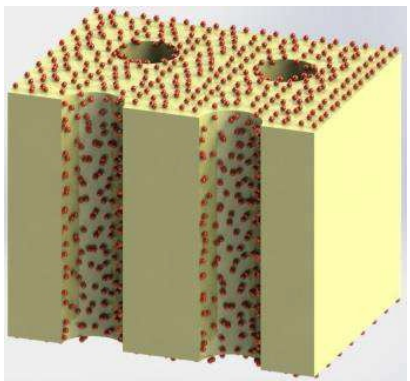

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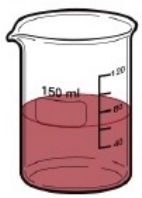

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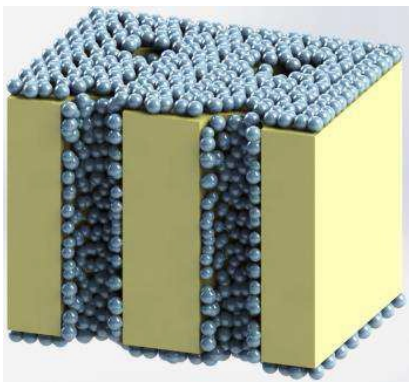

Initial tube growth

Images of templates: *ECS Trans.* **64** (31), 39-48 (2015)

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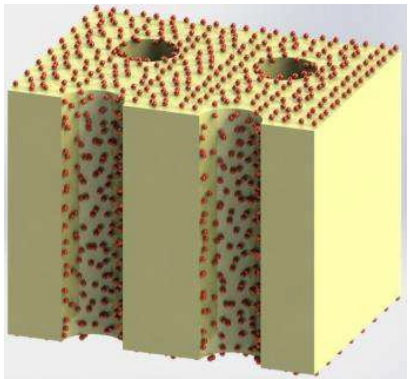

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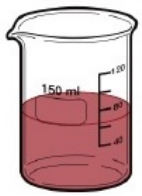

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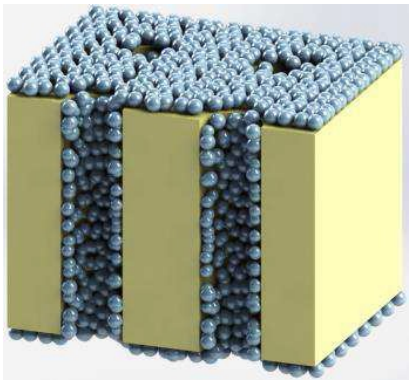

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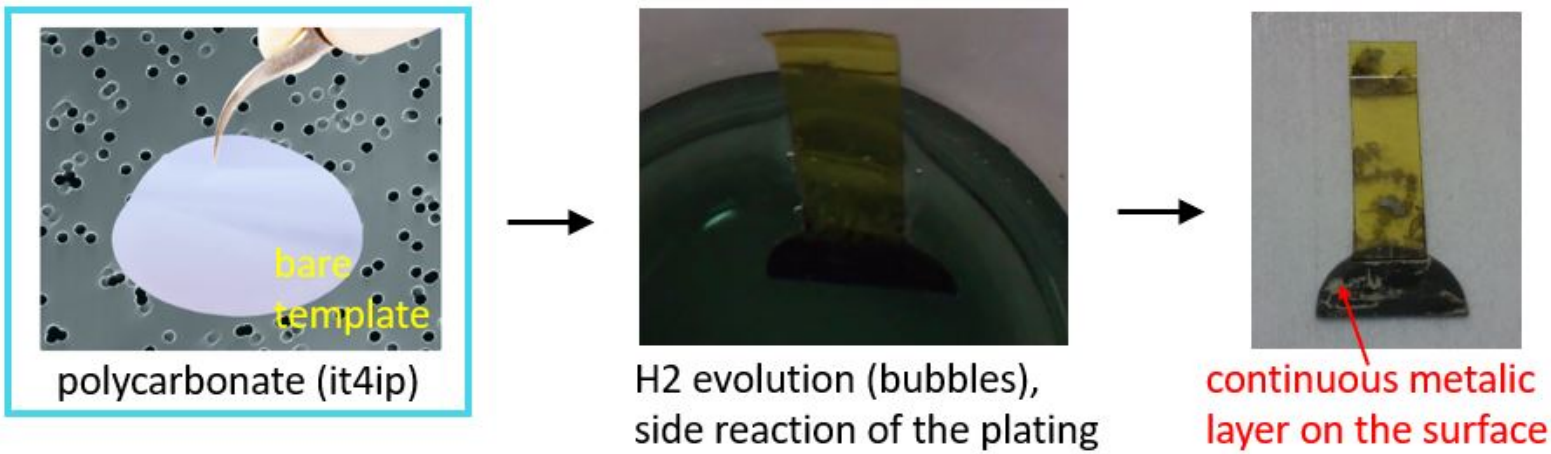
Obtaining individual nanotubes:

- Removal of top/bottom layer (mechanical / ion polishing)
- Template dissolution
- Purification of solution with nanotubes, organic solvents
- Transfer onto a substrate (Si) – micropipette

Our depositions: CoNiB, CoB

CoNiB tubes: Schaefer et al., *RSC Adv.* **6**, 70033-70039 (2016)

room temperature: $\approx$ 1.5 nm/min

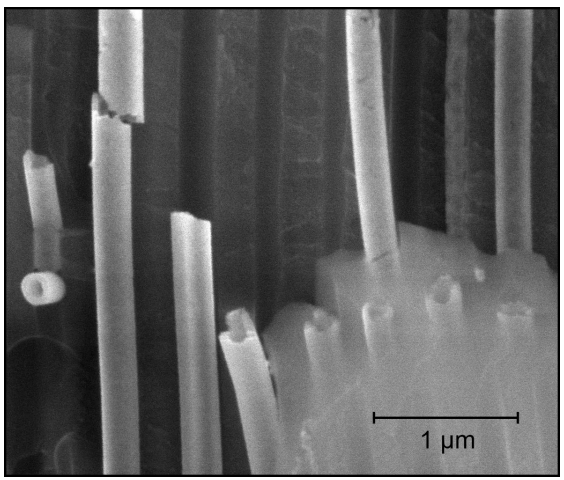


CoB: nominal diameter 100 nm and 200 nm
CoNiB: nominal diameter 200 nm

Template dissolution

- alumina template in strong acids or bases (NaOH, KOH)
- polycarbonate in non-polar solvents (DMF – DiMethylFormamide)

Our tubes – electron microscopy micrographs



CoNiB (2) in alumina

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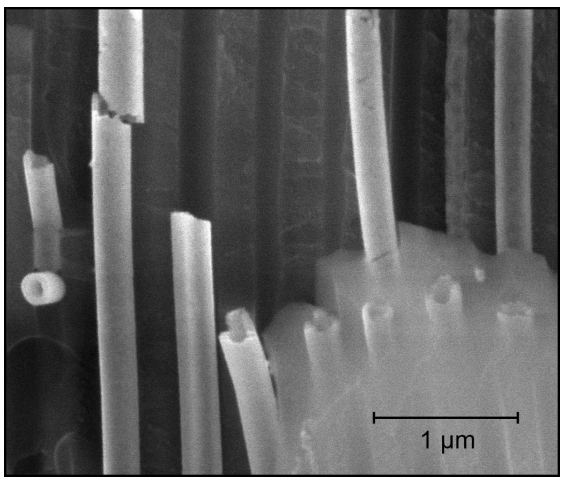

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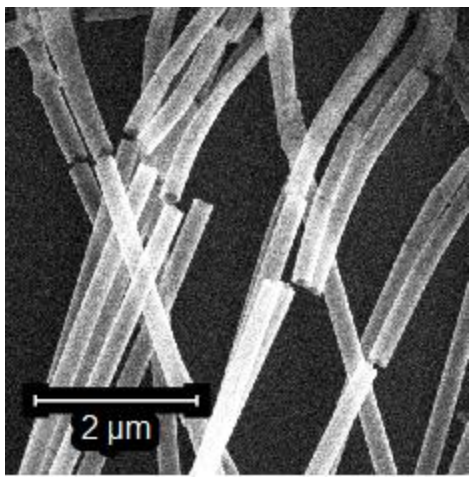

CoB (5) on Si

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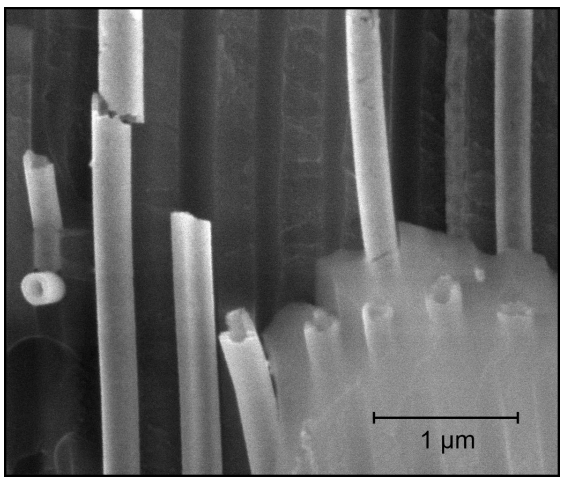
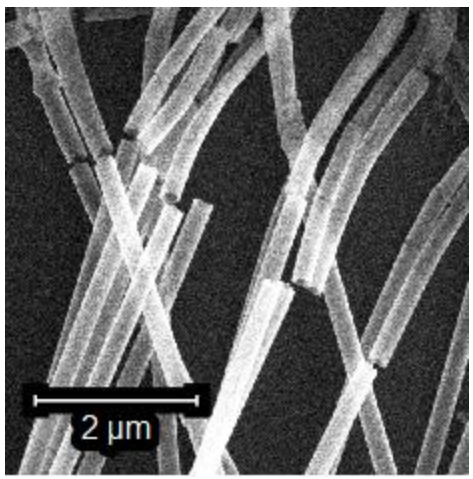
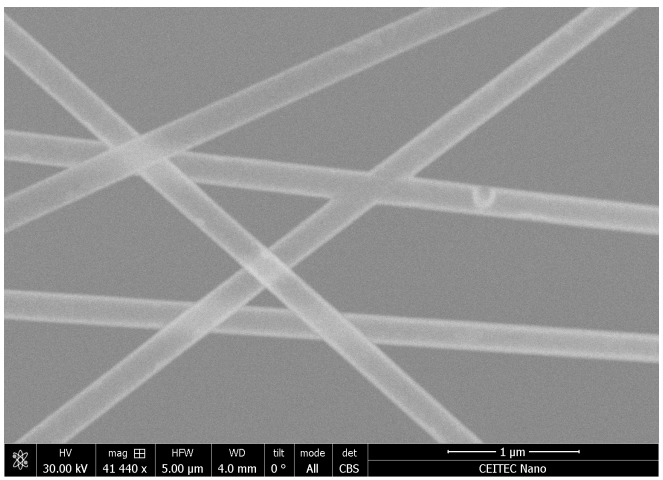


CoNiB (2) in alumina

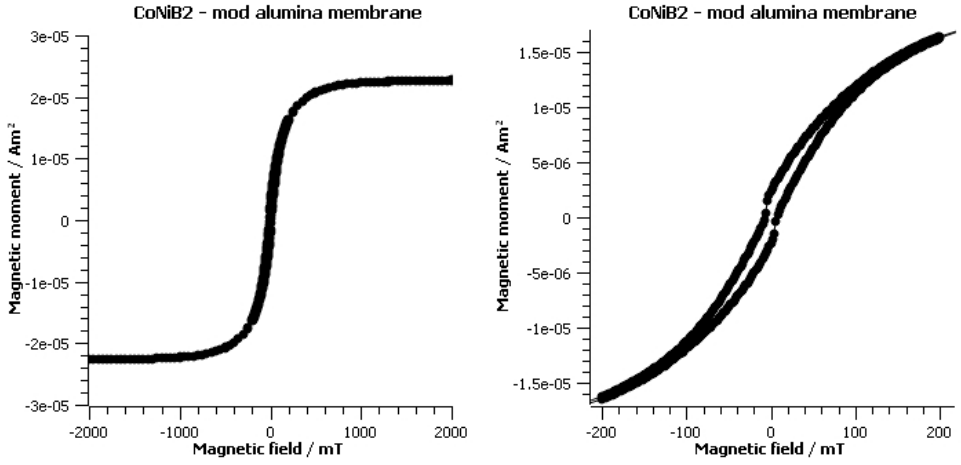


CoB (5) on Si



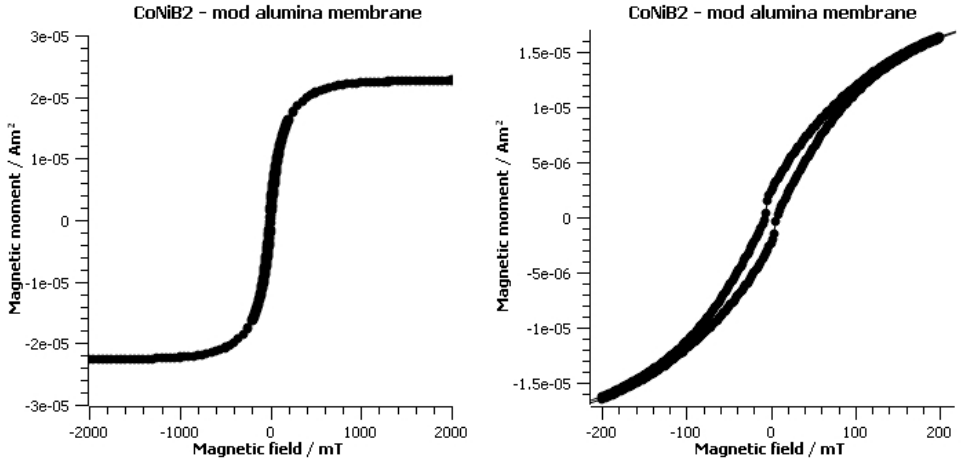
CoNiB (3) on Si

CoNiB tubes in **alumina** template [CoNiB 2]

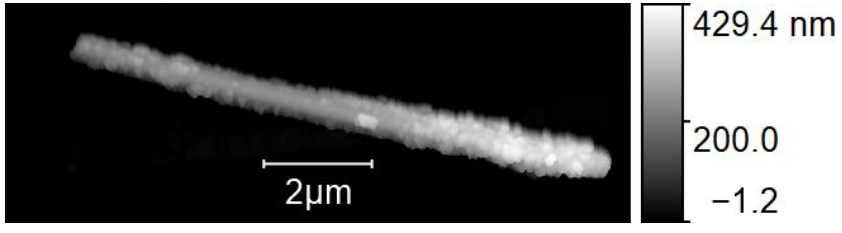


Magnetometry (VSM) on tube array (in template), field $\perp$ to tube axes

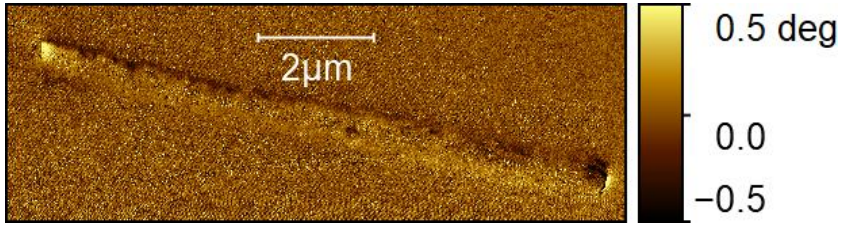
CoNiB tubes in **alumina** template [CoNiB 2]



Magnetometry (VSM) on tube array (in template), field $\perp$ to tube axes



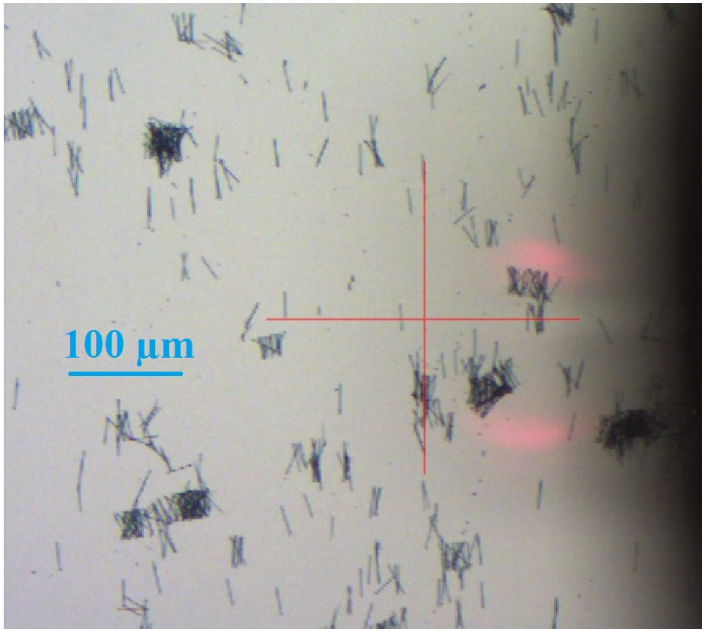
AFM, topography



MFM, 'magnetic poles'

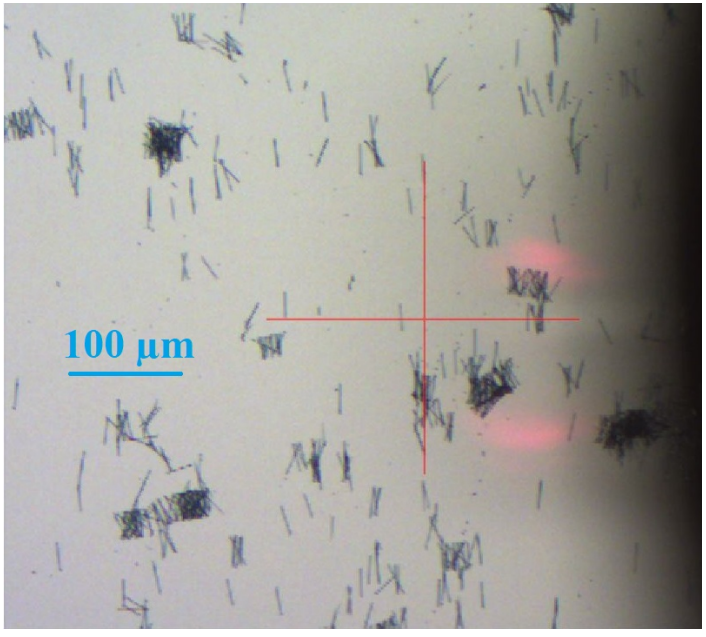
- diameters 200-300 nm (nominal template diamater 180 nm)
- dirty (**NaOH etching** – template + NaOH residuals, oxidation?)
- axial magnetization (like bar magnet)

CoNiB tubes in **polycarbonate** template [CoNiB 3]

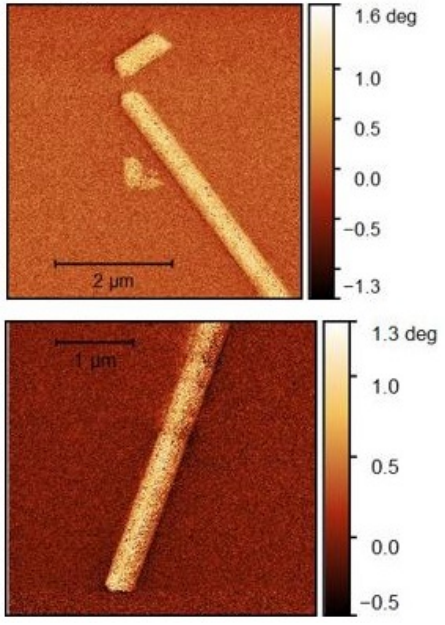


Optical image

CoNiB tubes in **polycarbonate** template [CoNiB 3]

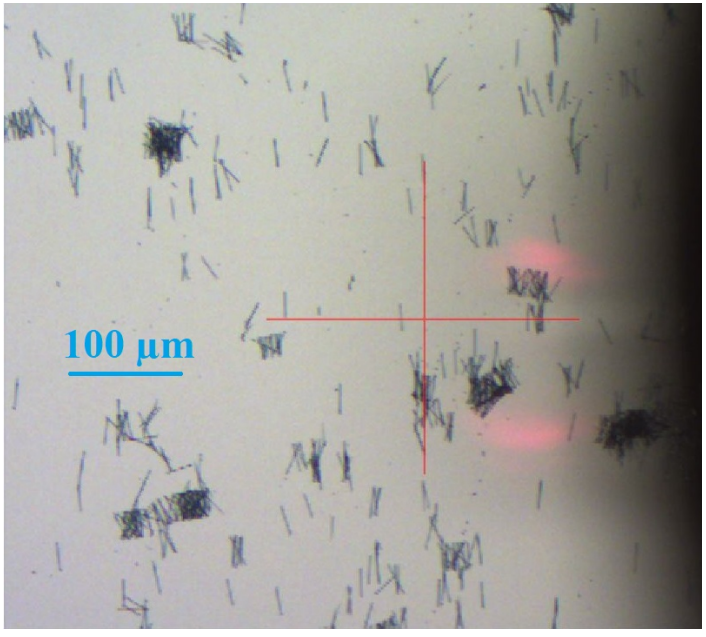


Optical image

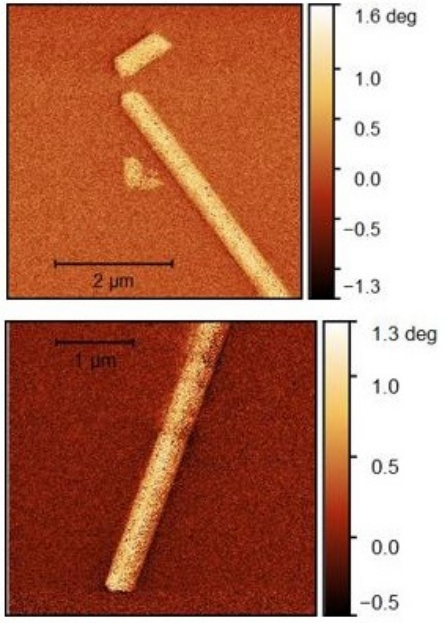


MFM, no mag. field

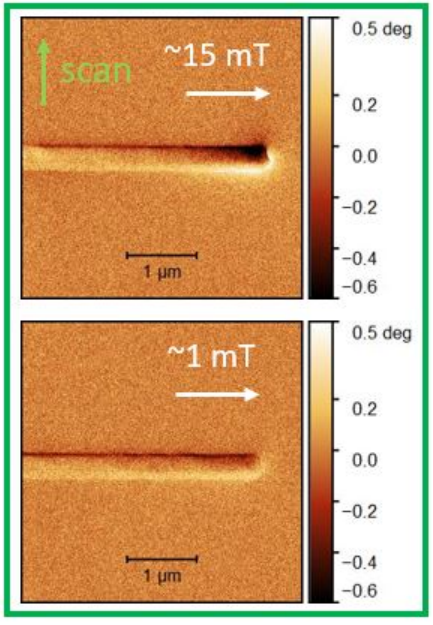
CoNiB tubes in **polycarbonate** template [CoNiB 3]



Optical image

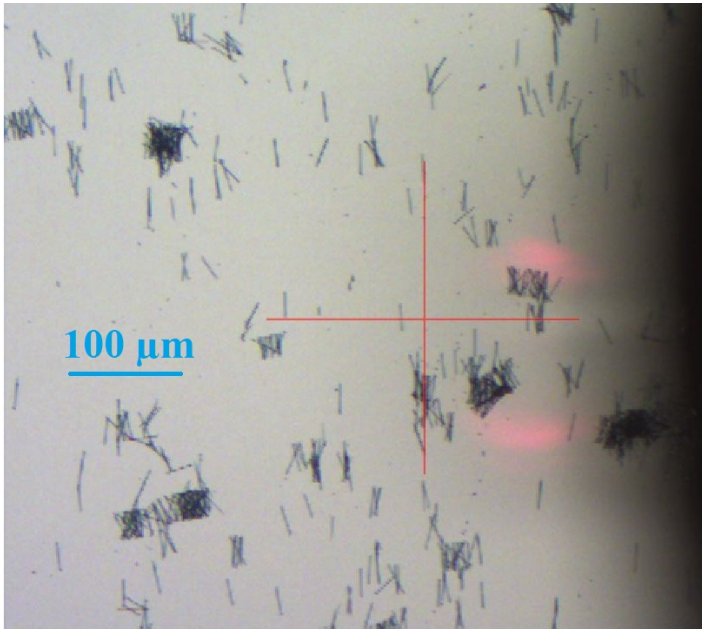


MFM, no mag. field

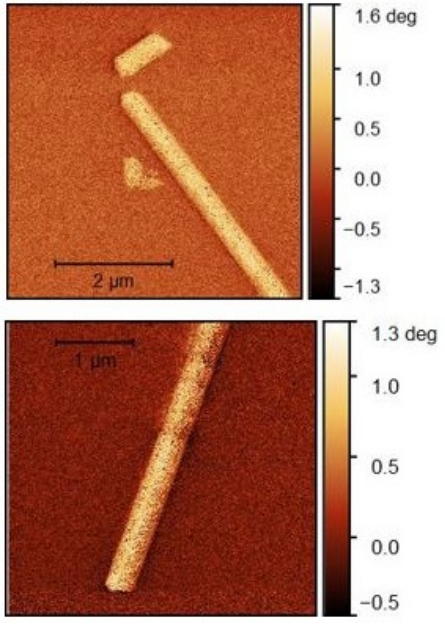


MFM, axial mag. field

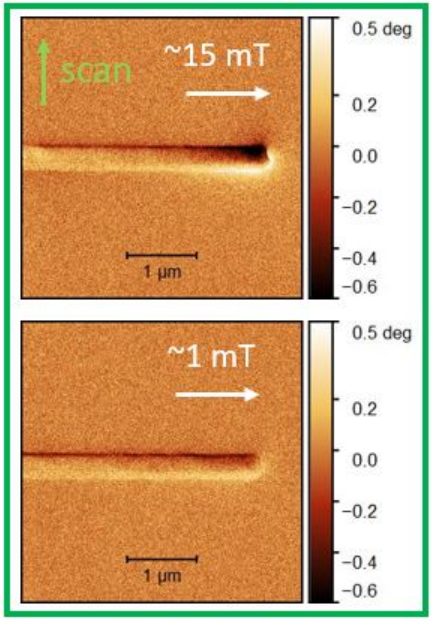
CoNiB tubes in **polycarbonate** template [CoNiB 3]



Optical image



MFM, no mag. field



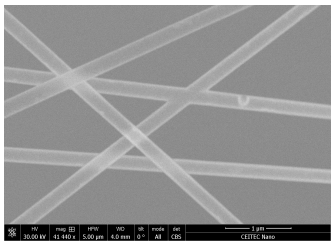
MFM, axial mag. field

- diameters 230-240 nm (nominal template diamater 200 nm)
- length up to 26 microns (template thickness)
- cleaner – rapid dissolution in organic solvent
- no or very weak magnetic signal at remanence
- MFM signal appears in ext. mag. field
- flux-closure domains at remanence (small stray field)

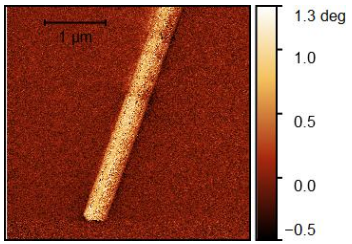
Summary

Electroless plated magnetic nanotubes

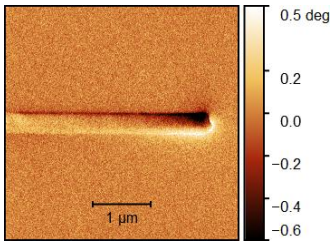
- CoB and CoNiB tubes (more uniform)
- polycarbonate template + organic solvent → cleaner tubes



SEM



MFM, no field



MFM, 15 mT axial

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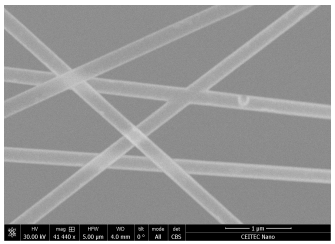
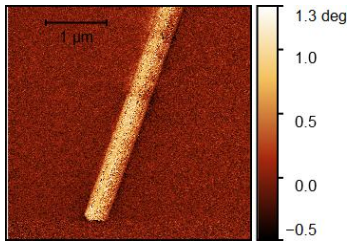
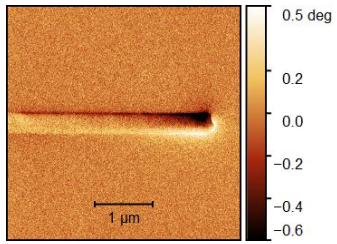


SEM



MFM, no field



MFM, 15 mT axial

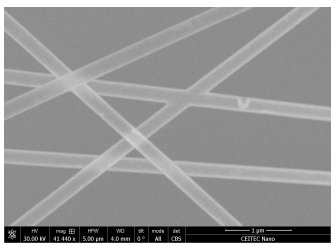
Magnetic force microscopy on individual CoNiB tubes

- preliminary: axial magnetization for tubes from alumina, flux-closure domain(s) for rapidly dissolved polycarbonate

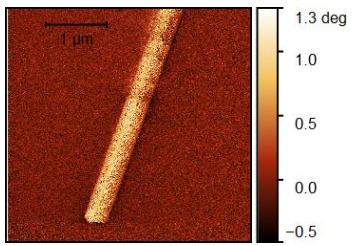
Summary

Electroless plated magnetic nanotubes

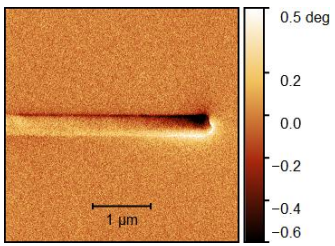
- CoB and CoNiB tubes (more uniform)
- polycarbonate template + organic solvent → cleaner tubes



SEM



MFM, no field



MFM, 15 mT axial

Magnetic force microscopy on individual CoNiB tubes

- preliminary: axial magnetization for tubes from alumina, flux-closure domain(s) for rapidly dissolved polycarbonate

Future

- Domain walls in tubes with flux-closure domains: in-field measurements (MFM), SEMPA (spin-SEM)?
- (local) magnetoresistance measurements
- Combining electroless magnetic layer + Ru spacer by ALD?

Acknowledgements

Thank you for your attention!

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YOUTH AND SPORTS

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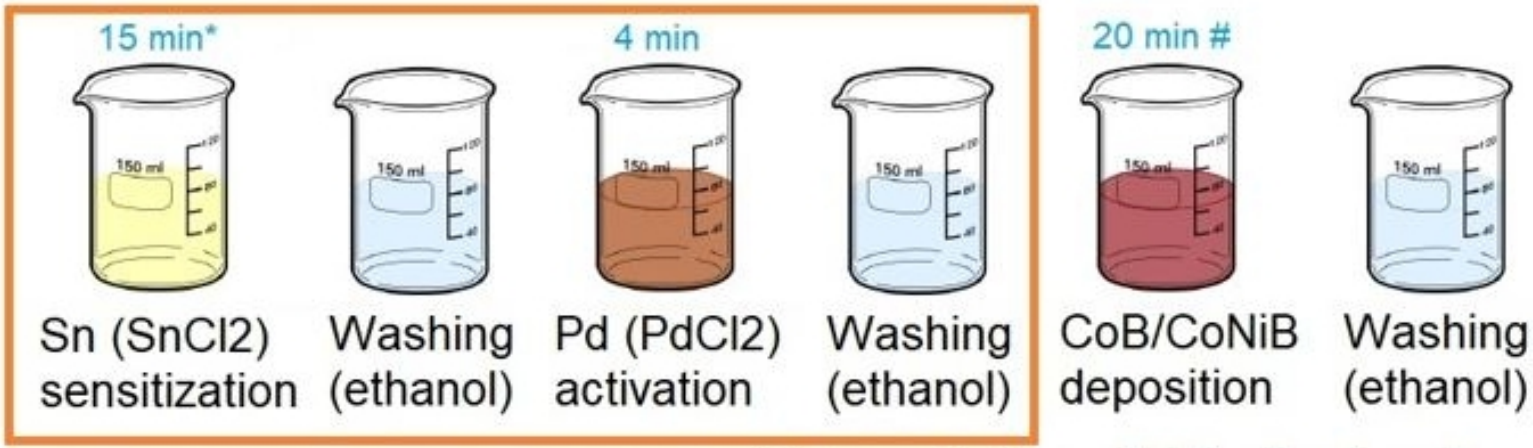
STAFF3d-spin project: http://magnetism.ceitec.cz/staff3d-spin/
(slides of presentations, updates, ...)

Electroless plating: Process scheme and photos



Substrate modification, repeated 3x

* first sensitization longer - 45 min

\# plating time depends on desired thickness