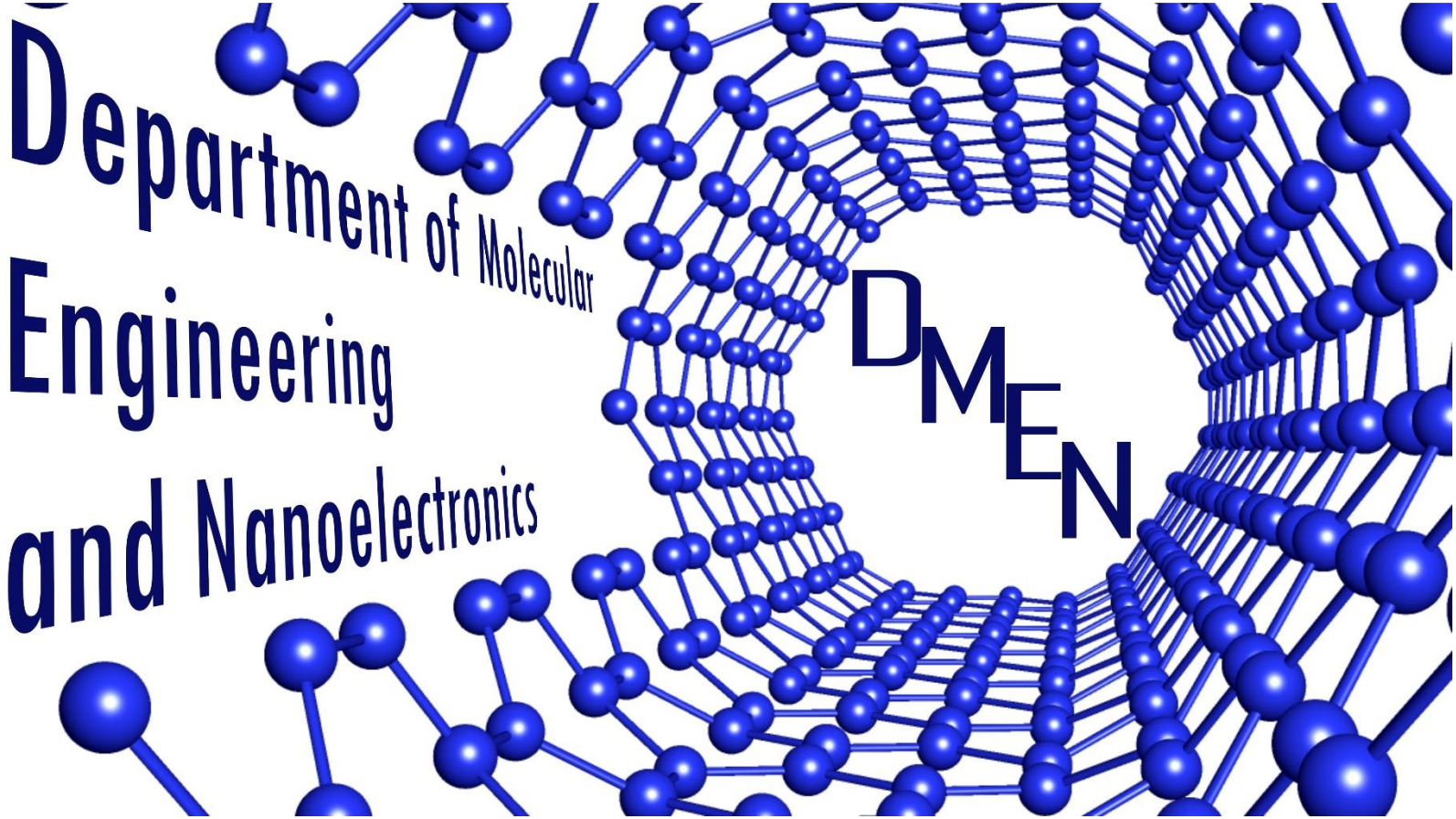
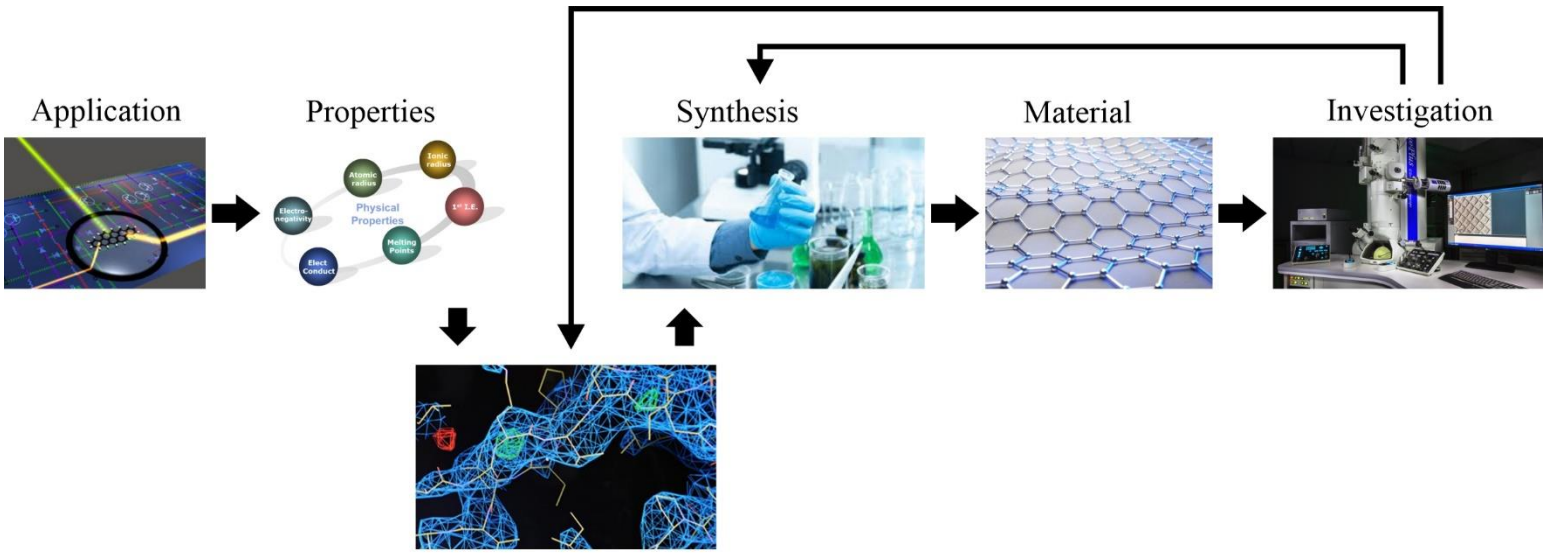
Dissolving ions and molecules in solids or what can we do employing molecular engineering

Lukasz Laskowski

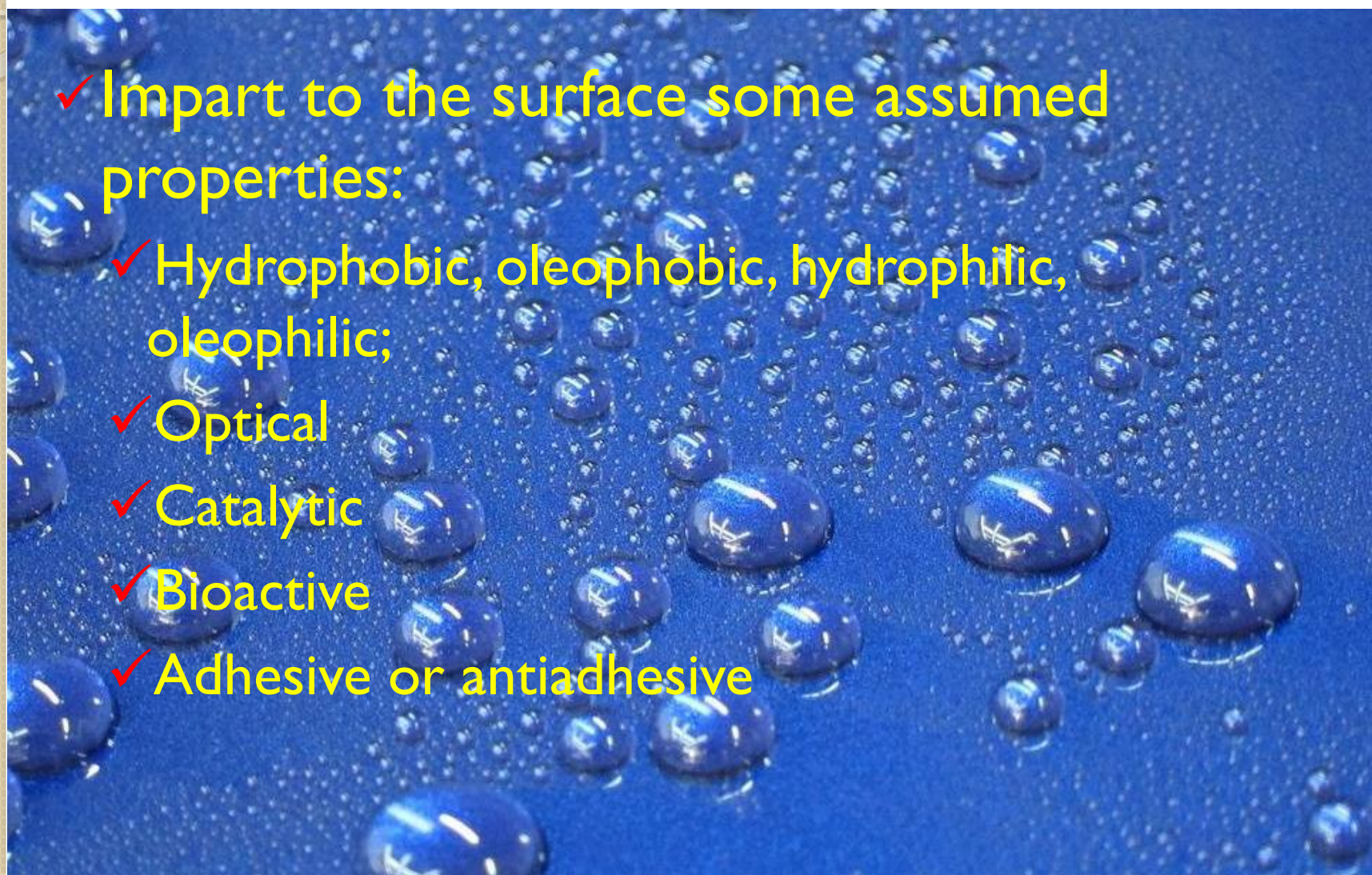


Physics *vs* Nanotechnology



Designing and molecular modeling

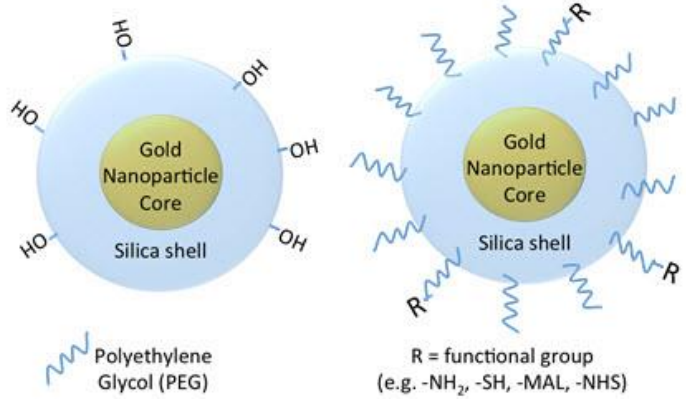
Surface modification: why

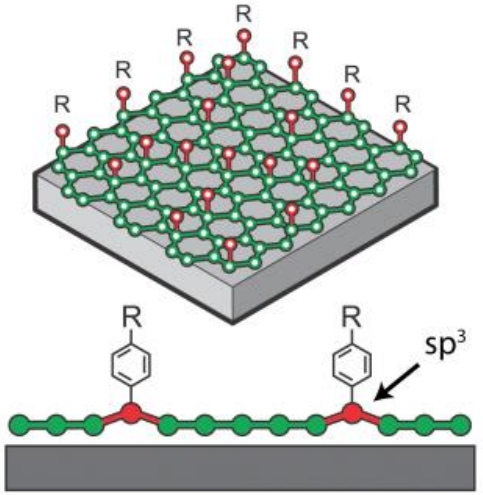


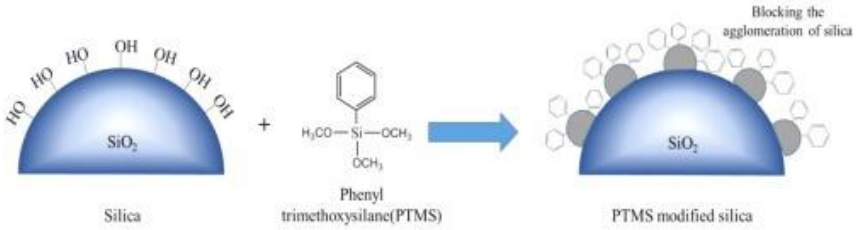
- ✓ Impart to the surface some assumed properties:
  - ✓ Hydrophobic, oleophobic, hydrophilic, oleophilic;
  - ✓ Optical
  - ✓ Catalytic
  - ✓ Bioactive
  - ✓ Adhesive or antiadhesive

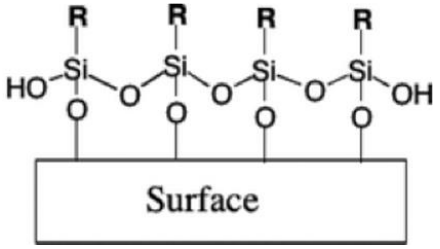
Surface modification: how?

- Attaching the proper functional units



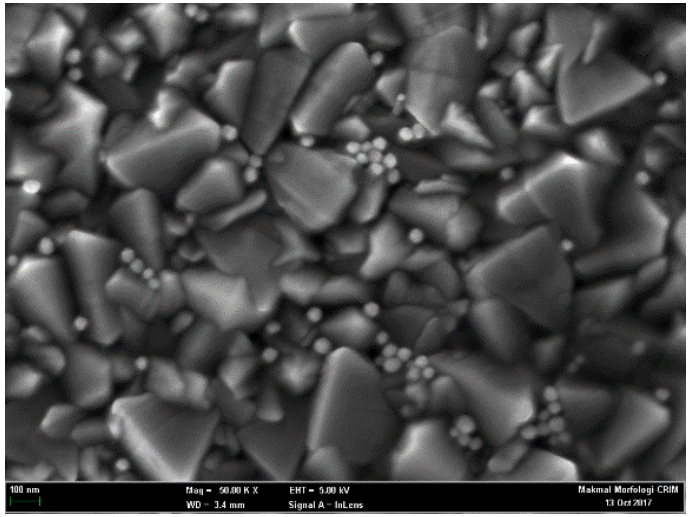


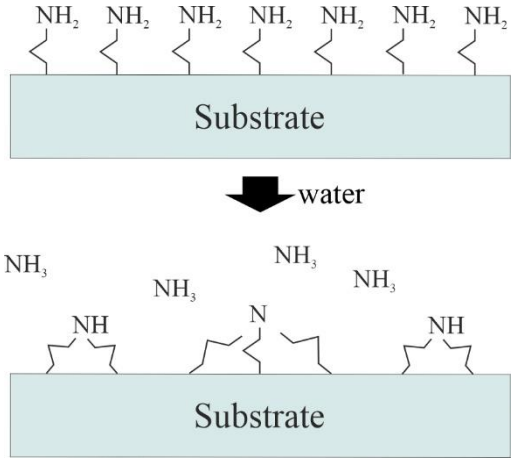




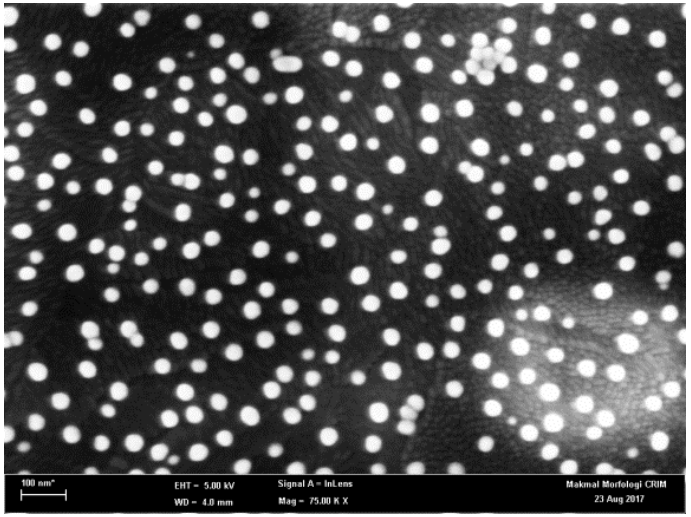
Some fails… let's figure out, why

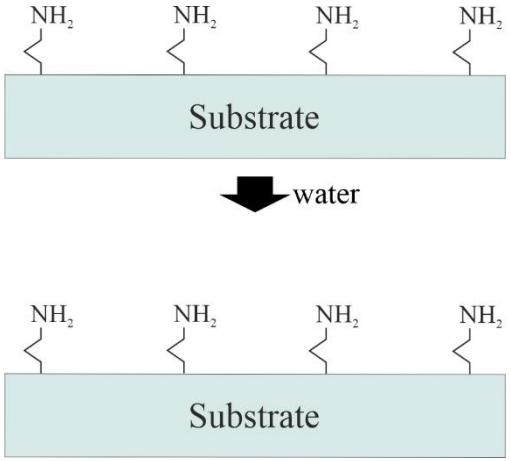
Full functionalization (tar and feather)





Precise functionalization (50% of anchoring units)





The key: PRECIESE functionalization!

- Tar and feather is a medieval technology
- Control the concentration of the functional units … like in a solution, a solid solution

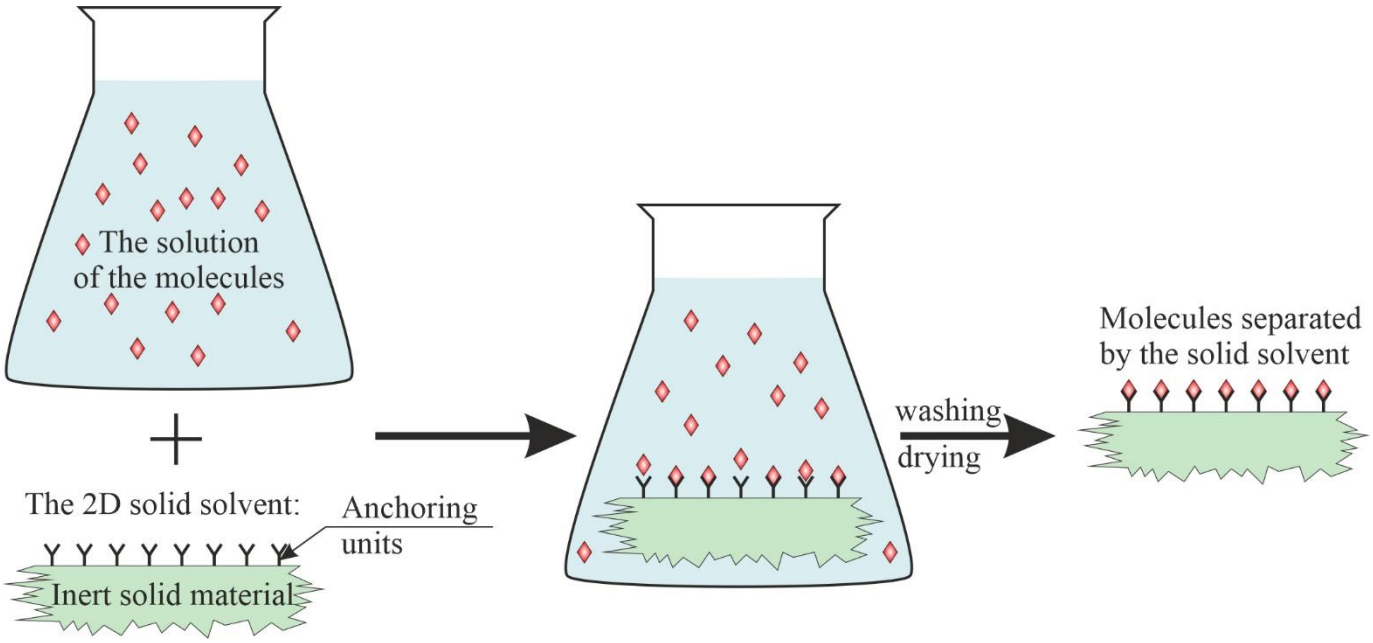
UPAC: *A crystal containing a second constituent which fits into and is distributed in the lattice of the host crystal*

[IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.]

- Control the distance between functional units
- Keep the molecules rigidly bonded

2D Solid Solvent

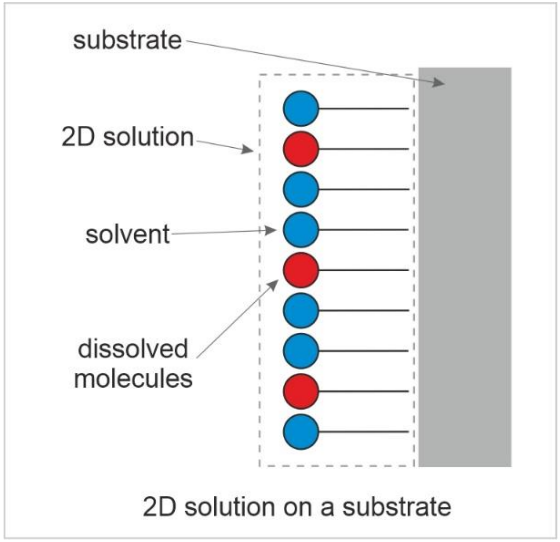
- The surface is covered by of anchoring units;
- A solid substrate with anchoring are connected and must be treated as one part – solid solvent;
- The functionalized surface is treated as a deposited layer of a 2D solution;
- The dissolving is easy: interaction of solvent and molecules

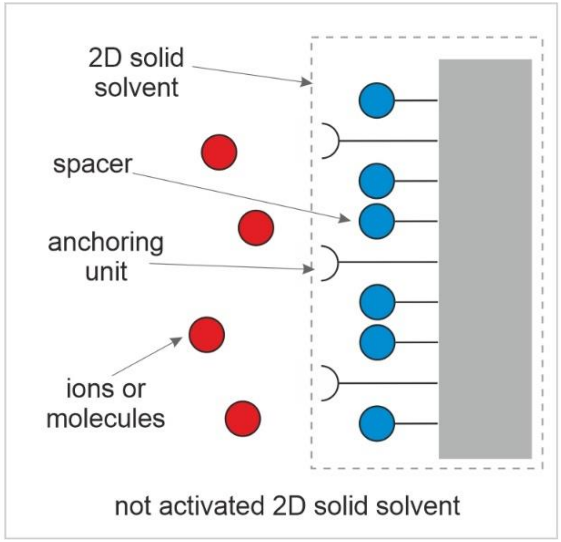


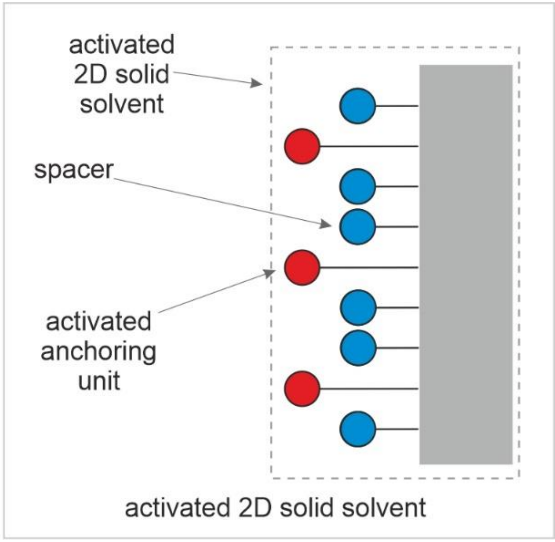
M. Laskowska , O. Pastukh, A. Fedorchuk, M.Schabikowski, P. Kowalczyk, M. Zalasiński , and Ł. Laskowski, Nanostructured SilicaWith Anchoring Units: The 2D Solid Solvent For Molecules And Metal Ions, Submitted to Int. J. Mol. Sci

How to keep the distances?

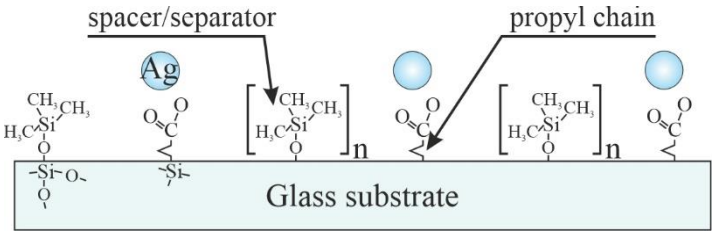
- Spacers/separators between anchoring units;
- Spacers are treated as an analogue of a solvent and activated anchoring units – as an analogue of a solute;
- The reaction of activation of anchoring units is treated as an analogue dissolving.

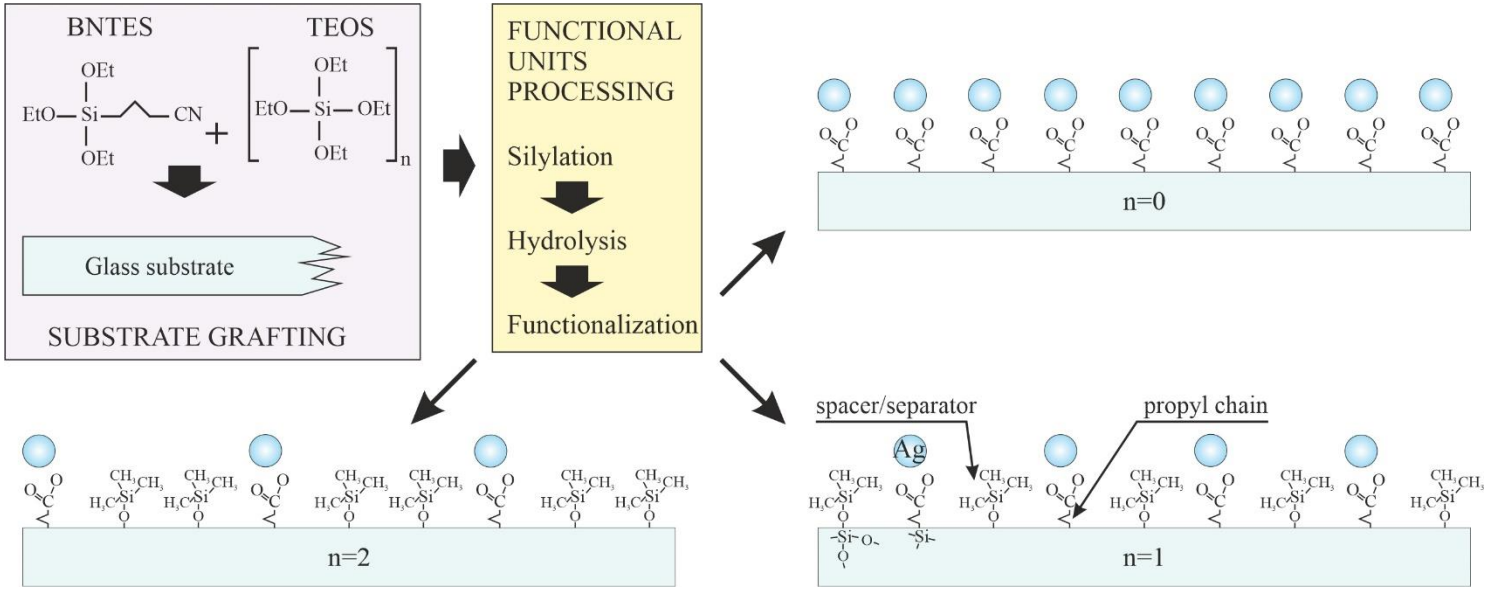


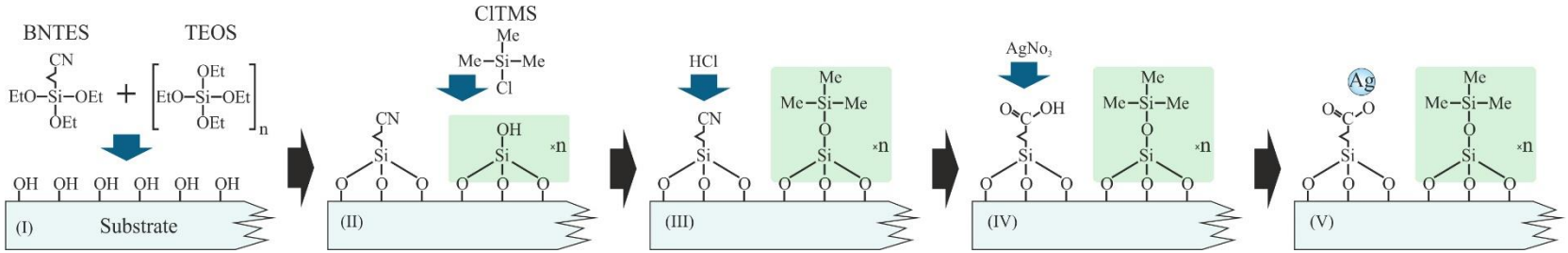




Can we do this?

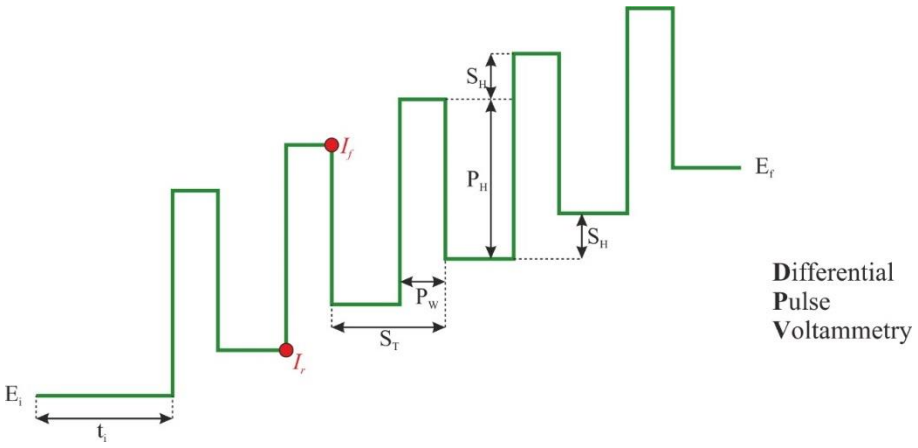


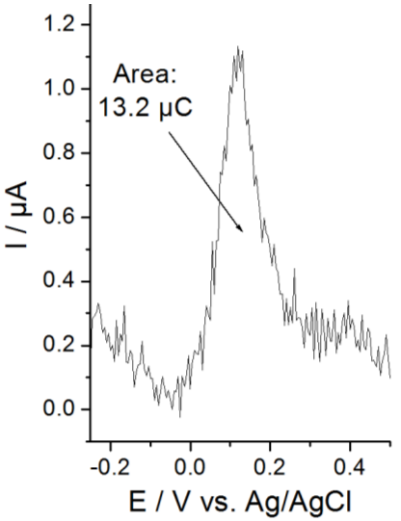


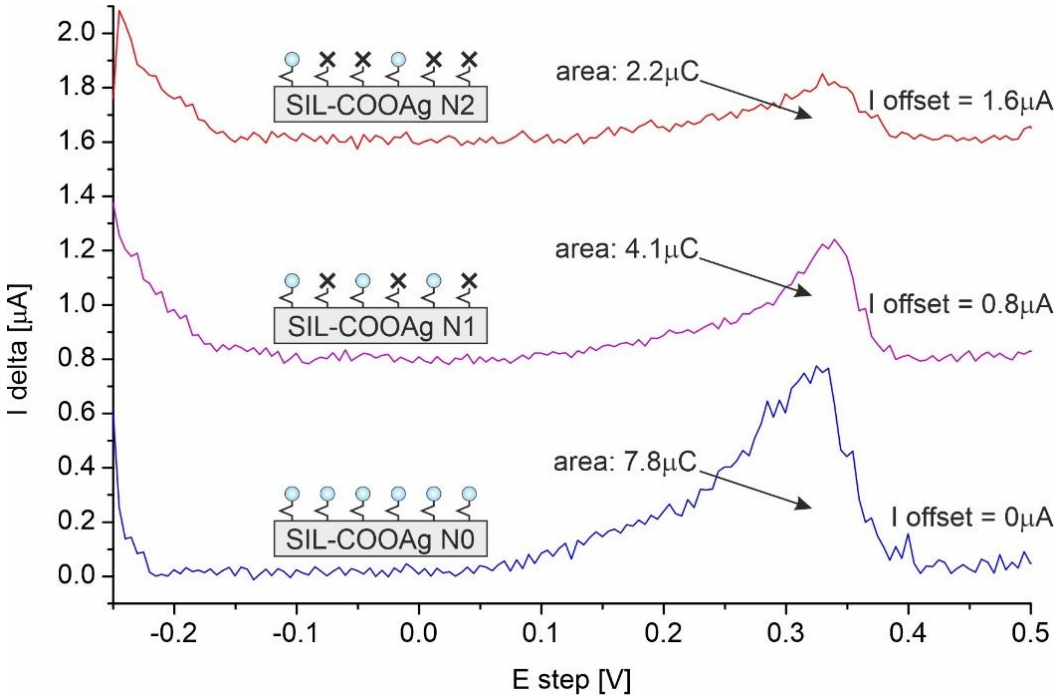


M. Laskowska, M. Oyama, I. Kityk, M. Marszałek, M. Dulski, Ł. Laskowski*, Surface functionalization by silver-containing molecules with controlled distribution of functionalities, Applied Surface Science, 481 (2019) 433-436

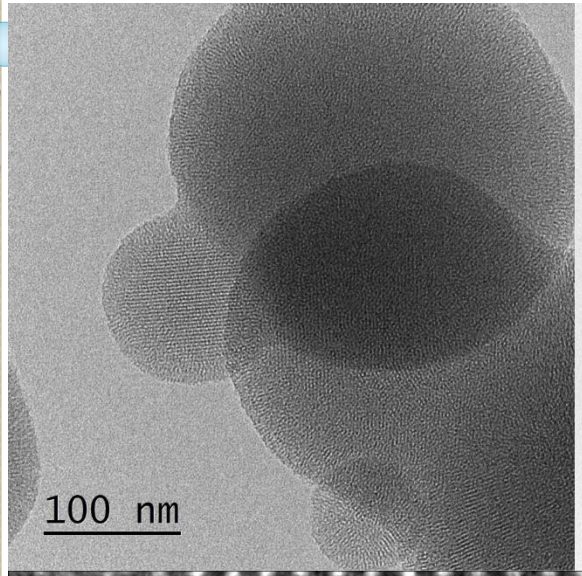
How to check the procedure?

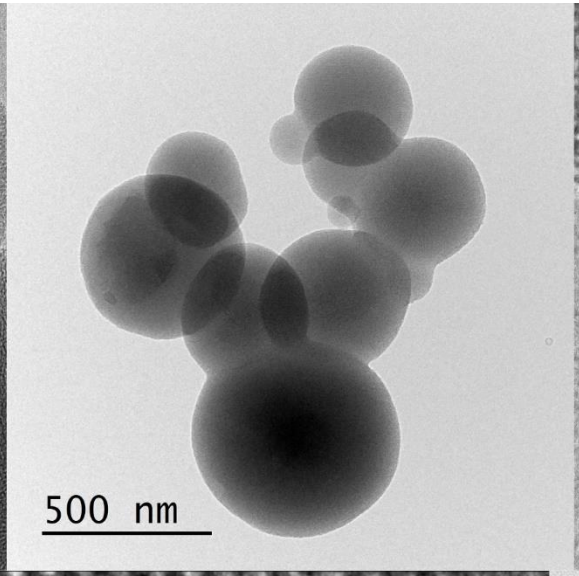


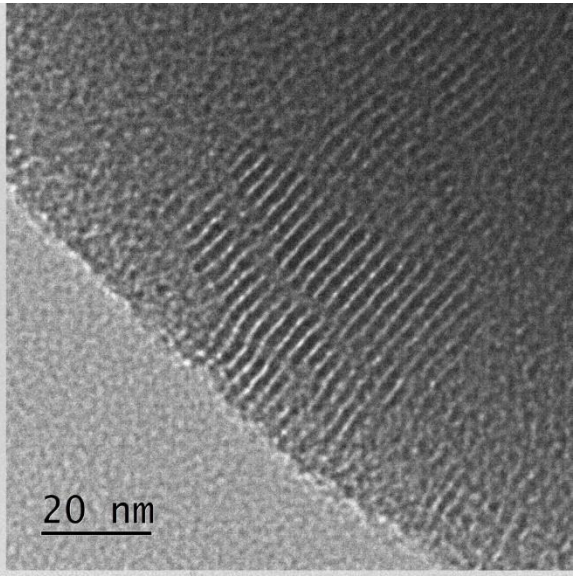


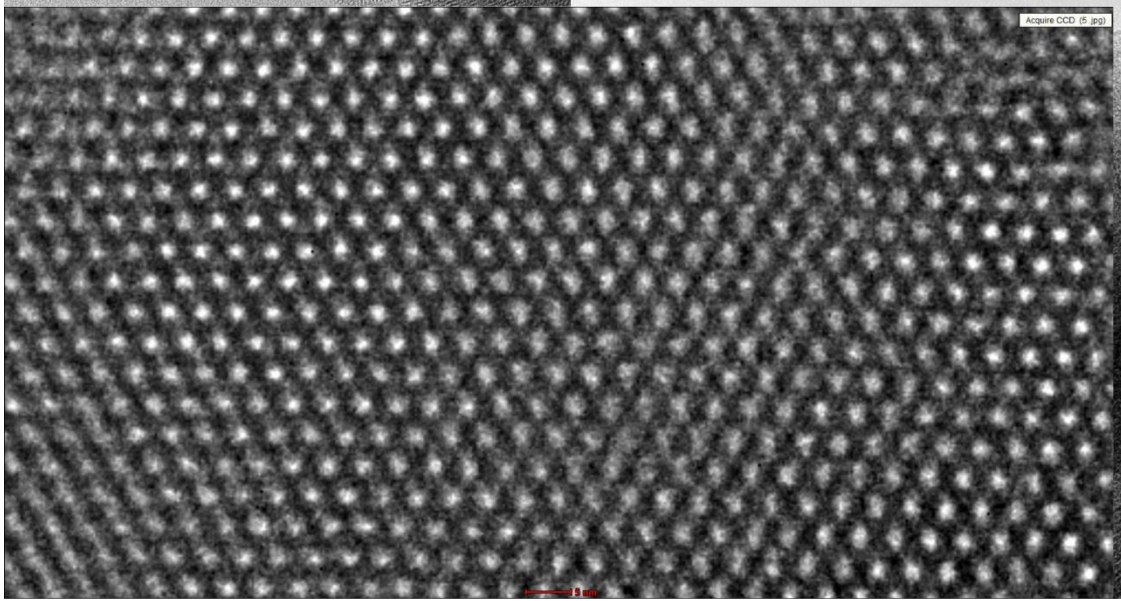


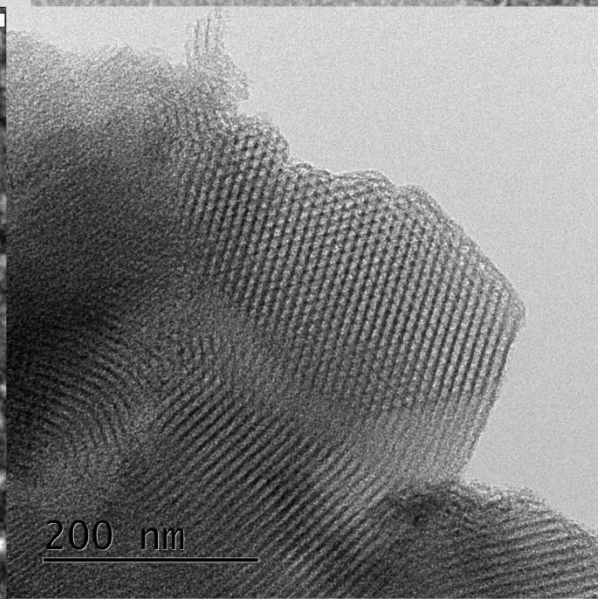
The surface does not have to be flat



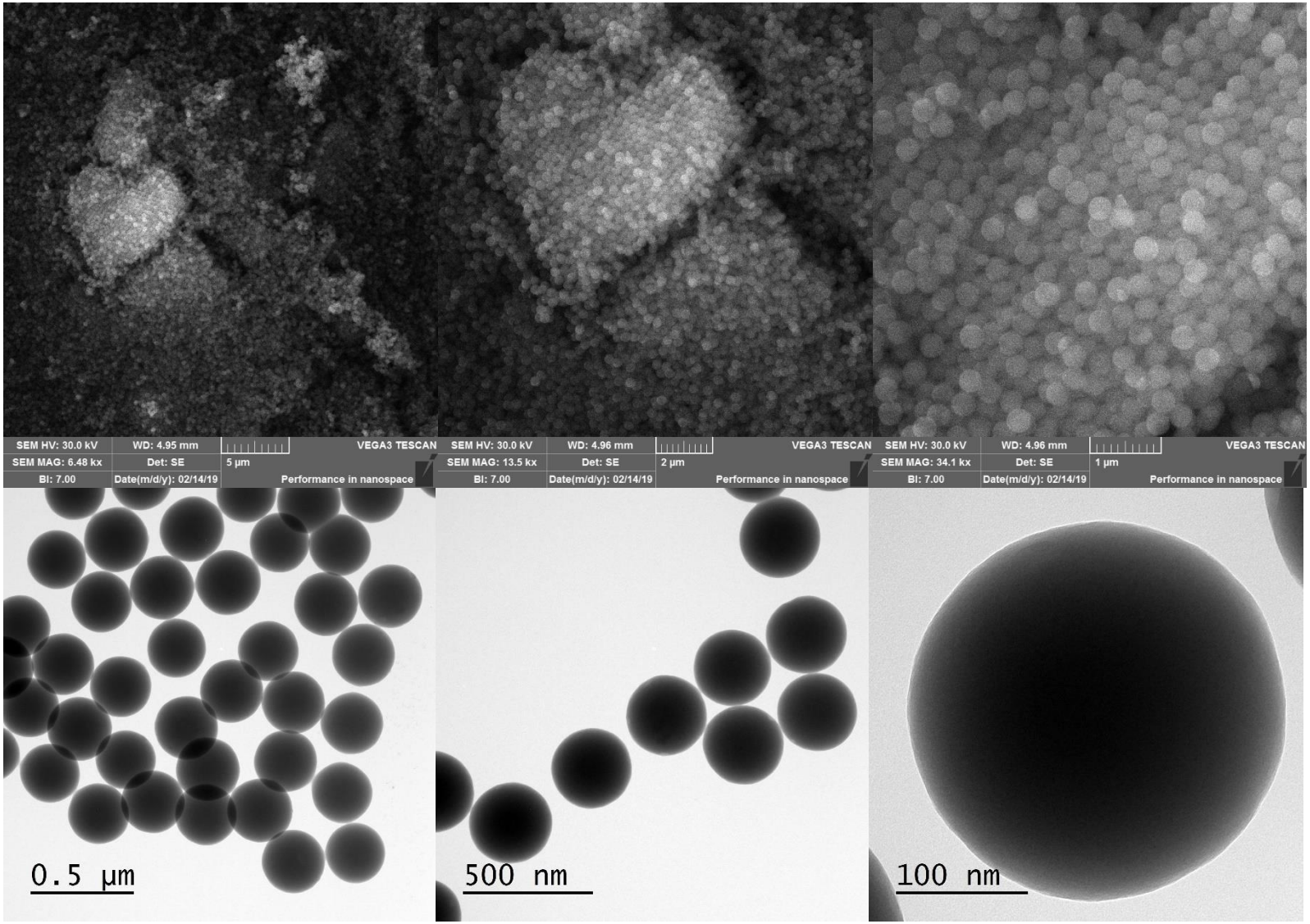




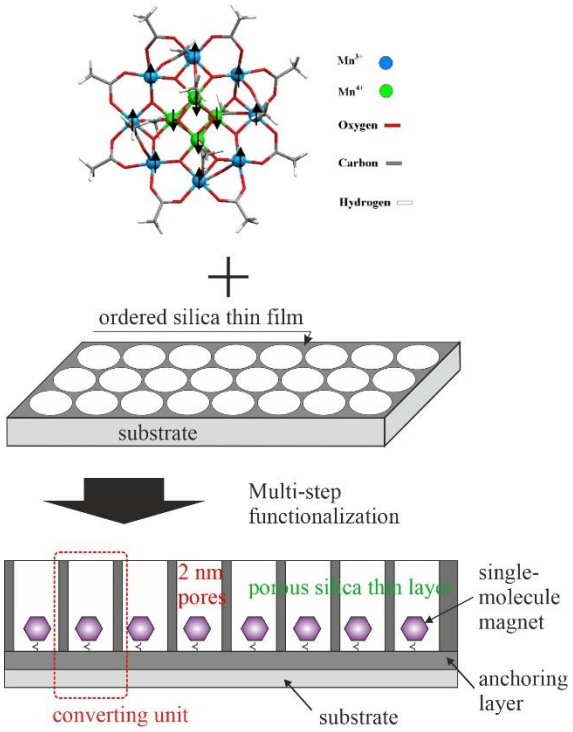


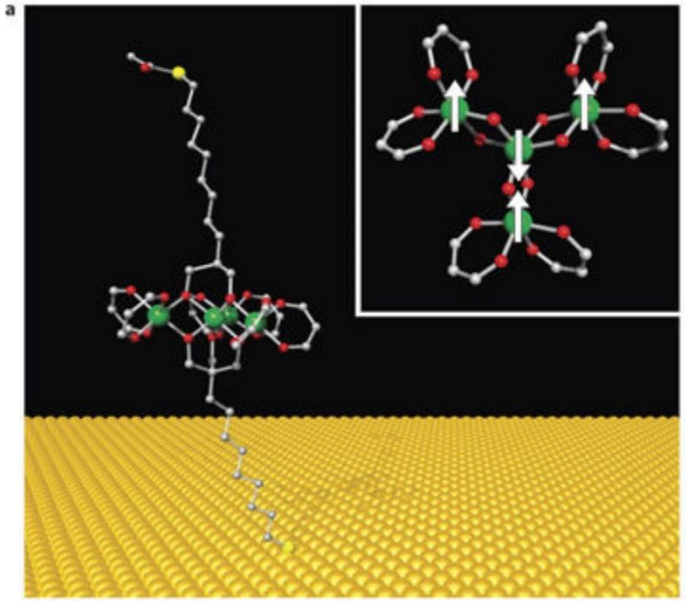


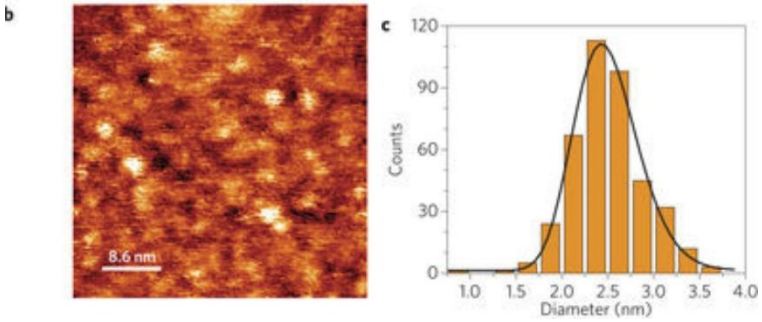
Spherical silica



The motivation







Cornia, A.; Gatteschi, D.; others. Magnetic memory of a single-molecule quantum magnet wired to a gold surface. *Nature materials* 2009, 8, 194–197.

Prof. Wulf Wulfhekel (Martin-Luther Universität Halle) wrote:

„I suggest you to use synchrotron radiation (XMCD) for this task. It can not see individual magnetic units but you can detect the magnetic moments of the ensemble relatively easy."

„You need to have atomically clean substrate"

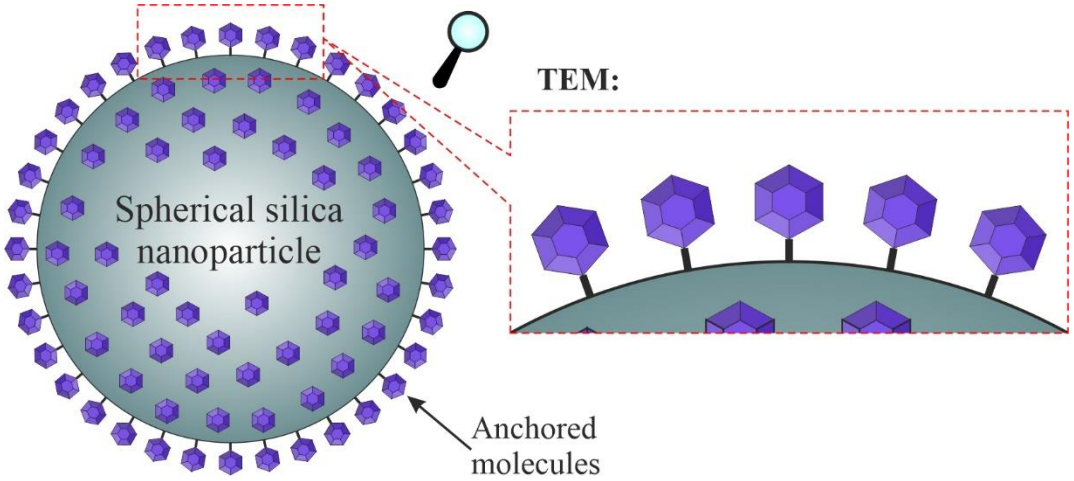
Ł. Laskowski, M. Laskowska, M. Dulski, M. Zubko, J. Jelonkiewicz, M. Perzanowski, N. Vila, A. Walcarius, Multi-step functionalization procedure for fabrication of vertically aligned mesoporous silica thin films with metal-containing molecules localized at the pores bottom, Microporous and Mesoporous Materials, 274 (2019) 356-362

Envy…

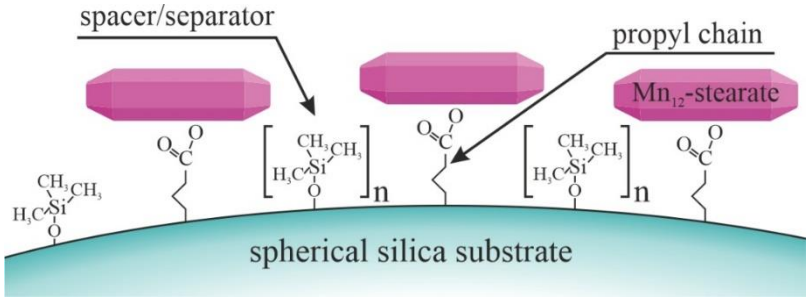
- Robust technology available in average chemical laboratory
- Allowing for easy manipulation of Mn_{12} single-molecule magnets, including control of their distribution (distances)
- Allowing for checking the magnetic properties of attached SMMs – checking if the single-molecule magnets is a magnet when is a single molecule

Ł. Laskowski, M. Laskowska, N. Vila, M. Schabikowski, A. Walcarius, Mesoporous Silica-Based Materials for Electronics-Oriented Applications, Molecules 24 (2019), 2395

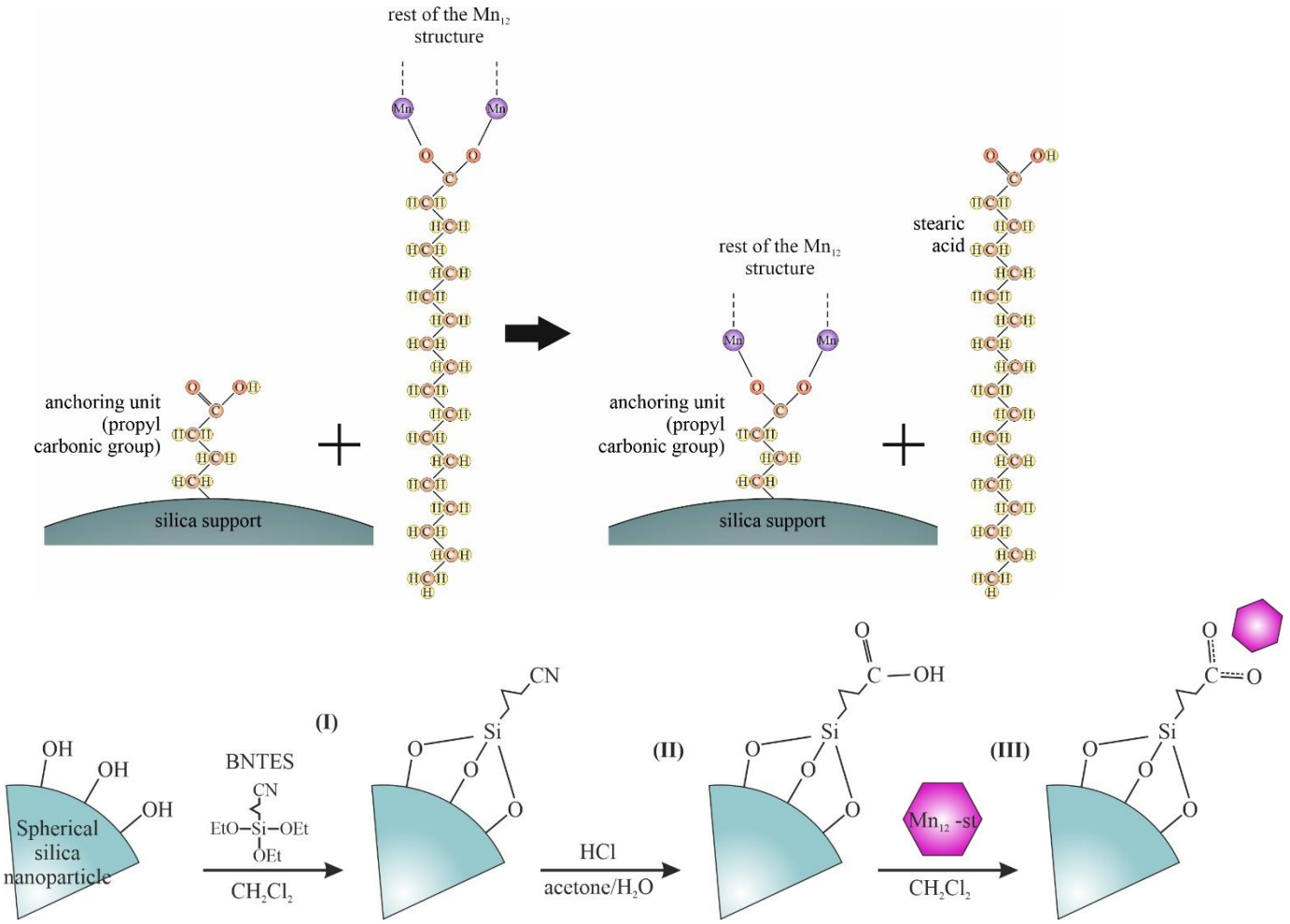
2D dissolving „in" spherical silica



- 2 nm Mn_{12} can be observed directly at the horizon employing TEM microscopy
- Magnetic properties can be easily measured: the material has a form of powder.
- The distribution control: spacers technology

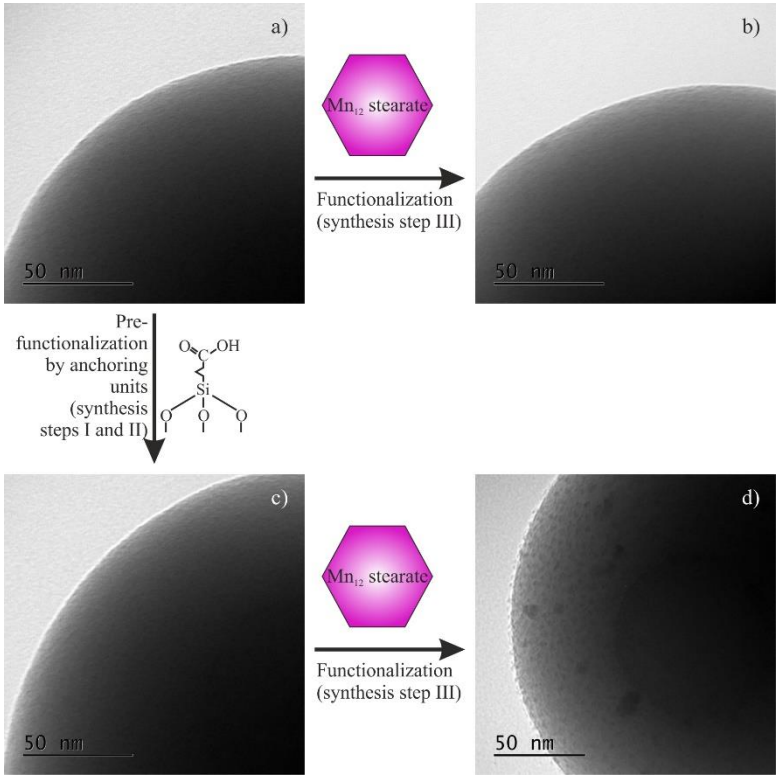


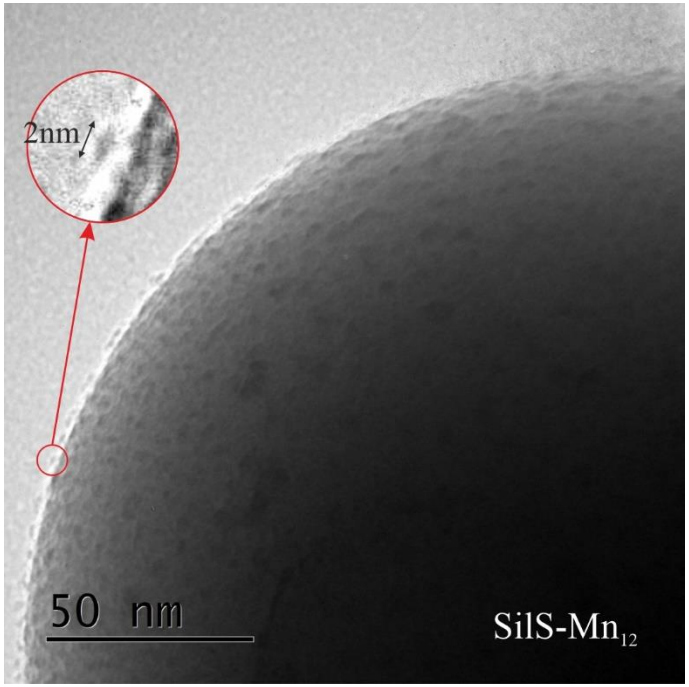
How to do this?

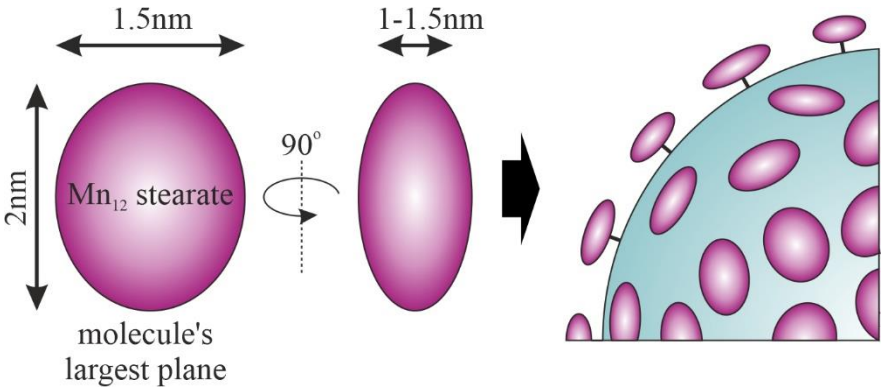


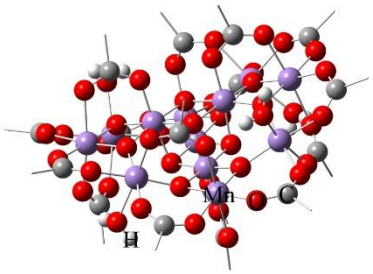
Ł. Laskowski, I. Kityk, P. Konieczny, O. Pastukh, M. Schabikowski, M. Laskowska, The Separation of the Mn12 Single-Molecule Magnets onto Spherical Silica Nanoparticles, Nanomaterials 9 (2019), 764-768

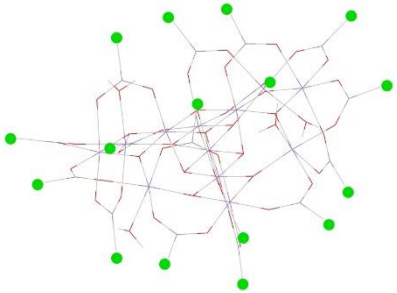
Does it works?



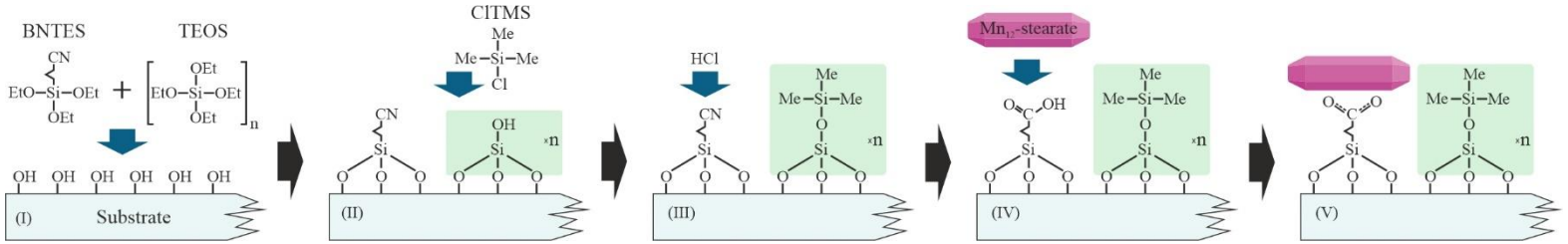


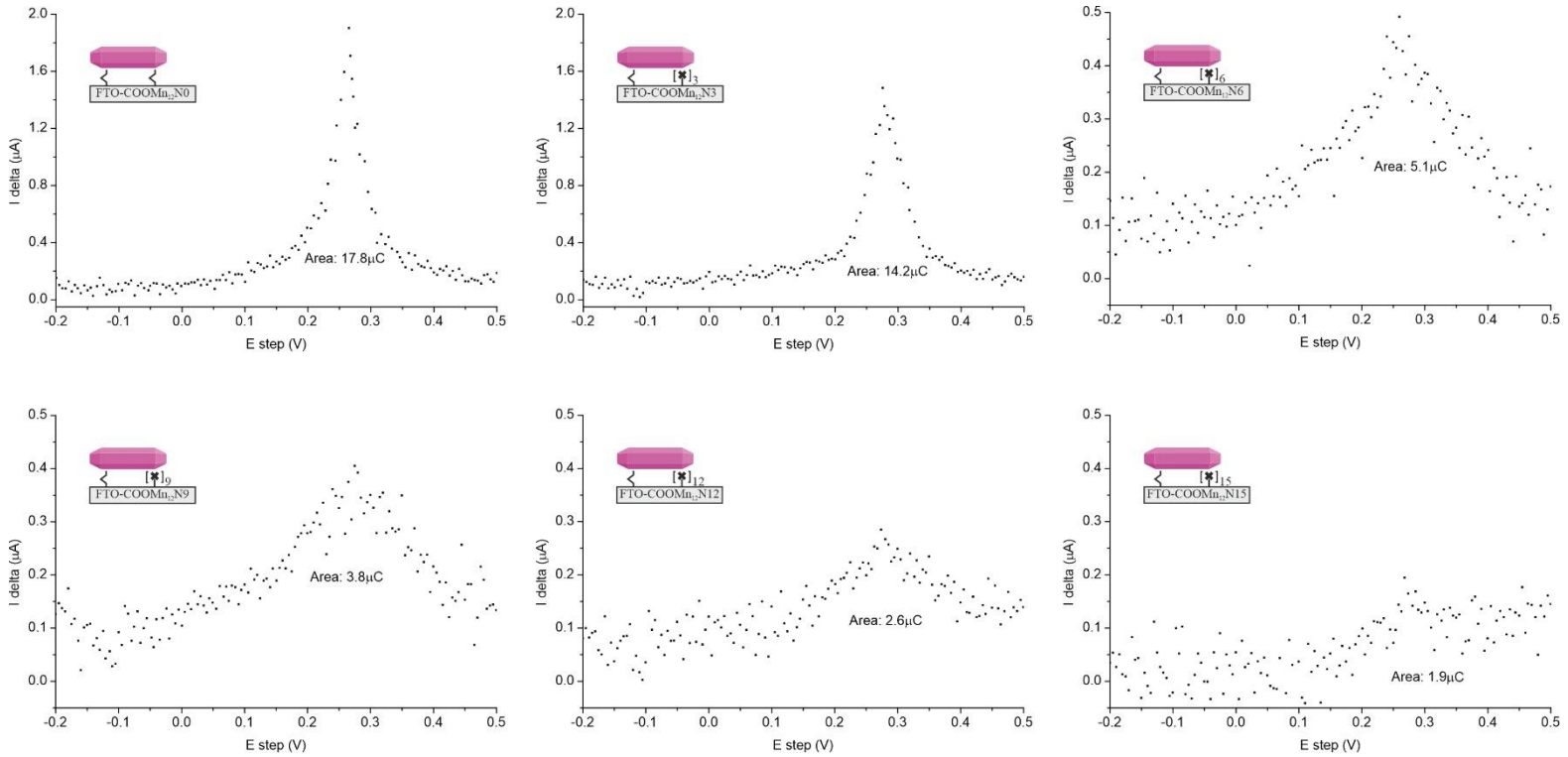






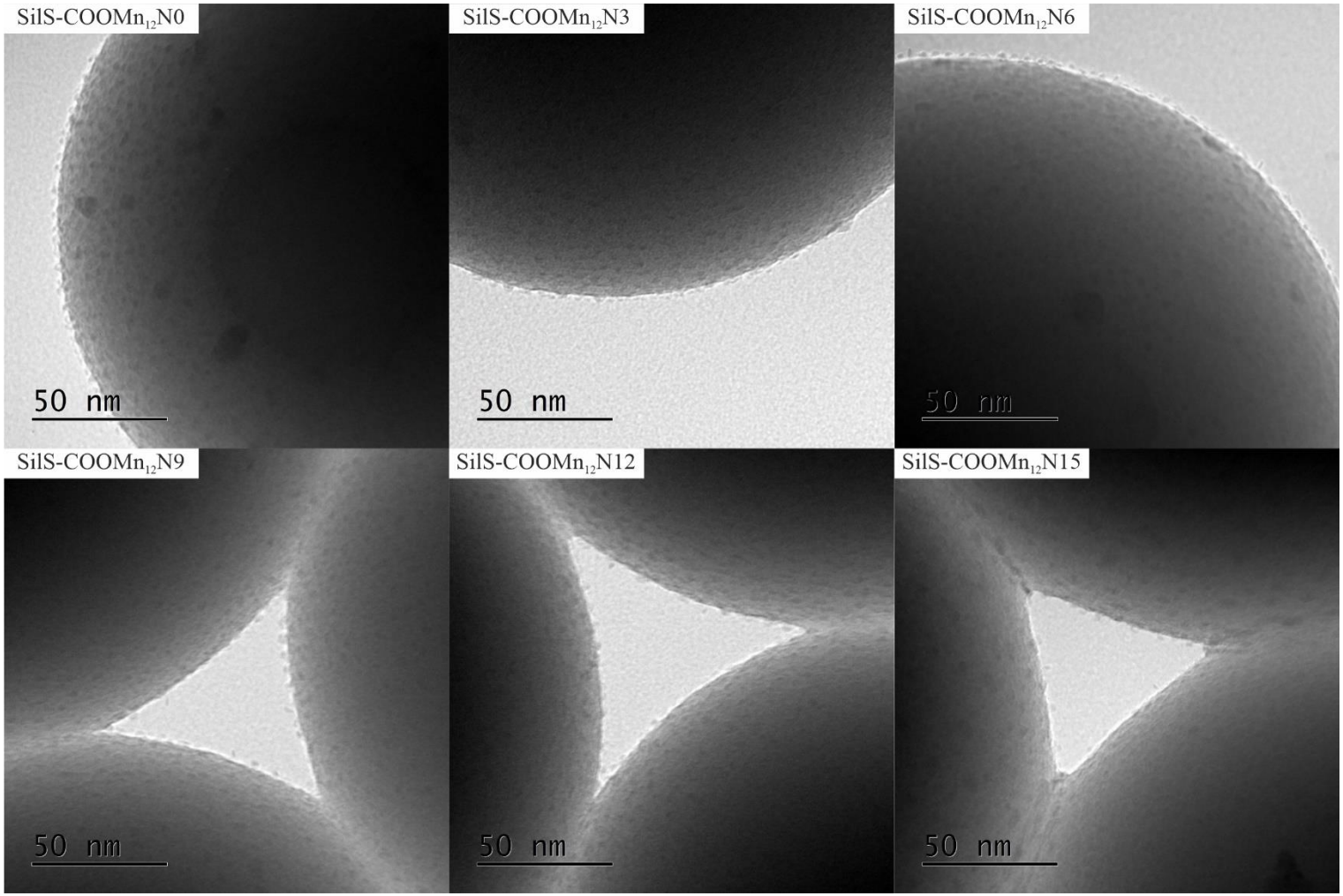
Let's try to modify the distribution of Mn_{12} …



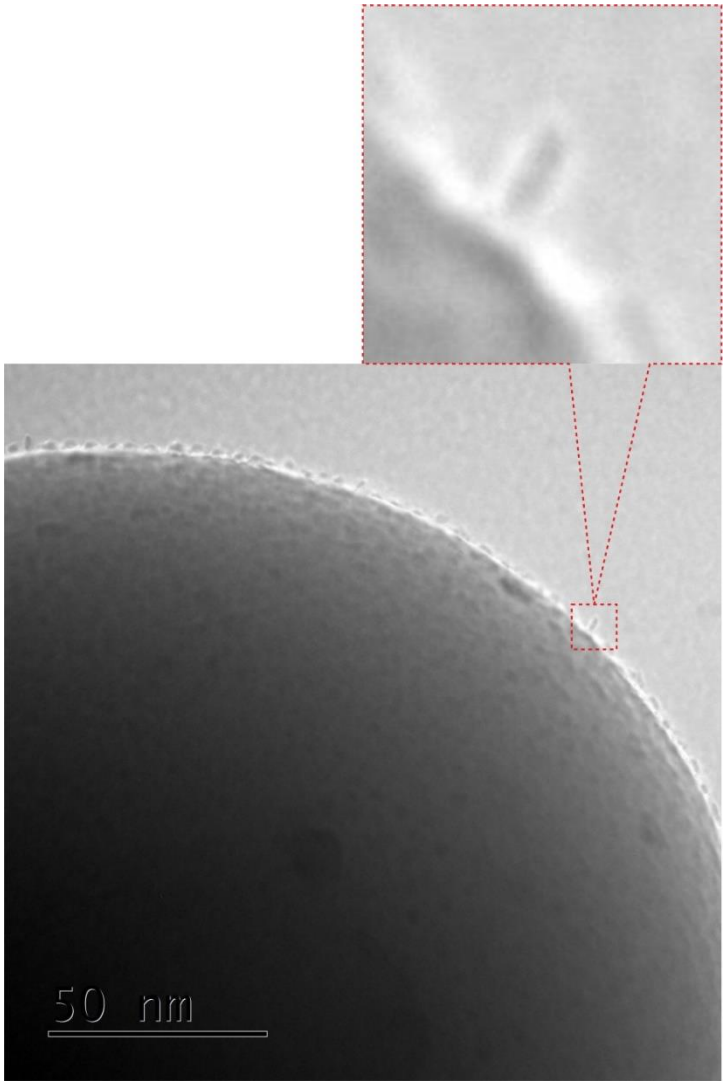


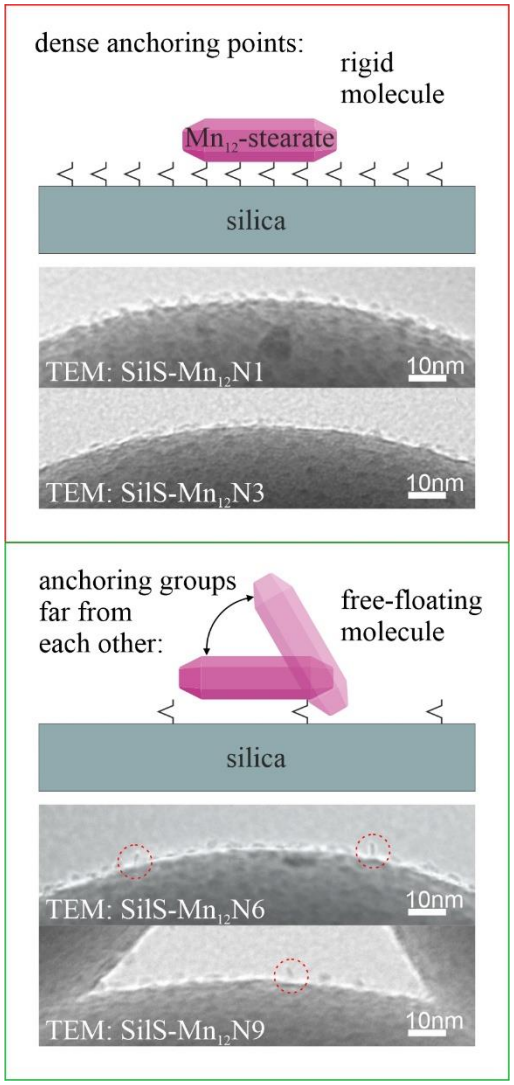
M. Laskowska, O. Pastukh, D. Kuźma, Ł. Laskowski, How to Control the Distribution of Anchored, Mn-12-Stearate, Single-Molecule Magnets, Nanomaterials 9 (2019), 1730

Some inconsistency…

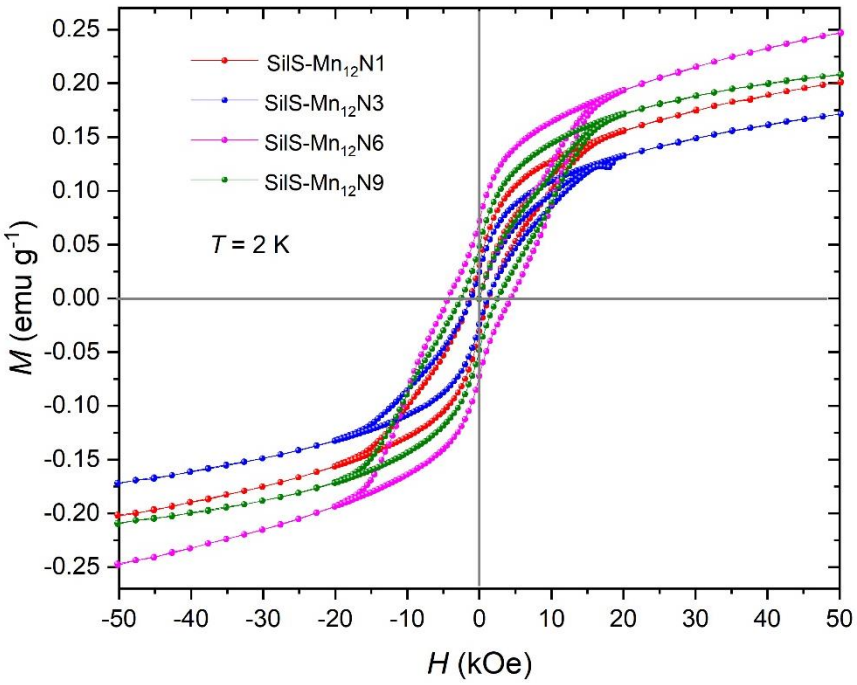


Maybe it is not an inconsistency?

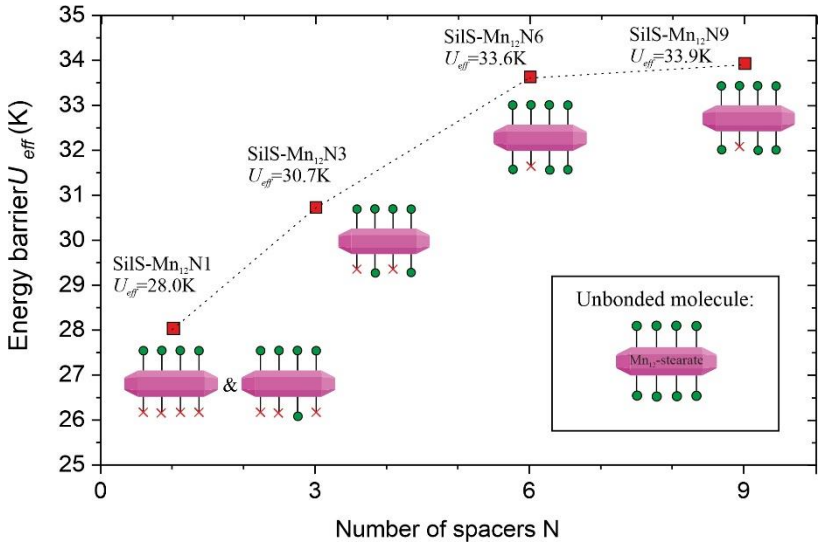




Did we prevent the SMMs from the surface Alzheimer disseise?



By assuming the different mobility (degrees of the freedom) of SMMs and different concentration of spacer units, all of the samples have shown preservation of hysteretic magnetic behaviour and slow relaxation properties, characteristic for such Mn_{12} complex.

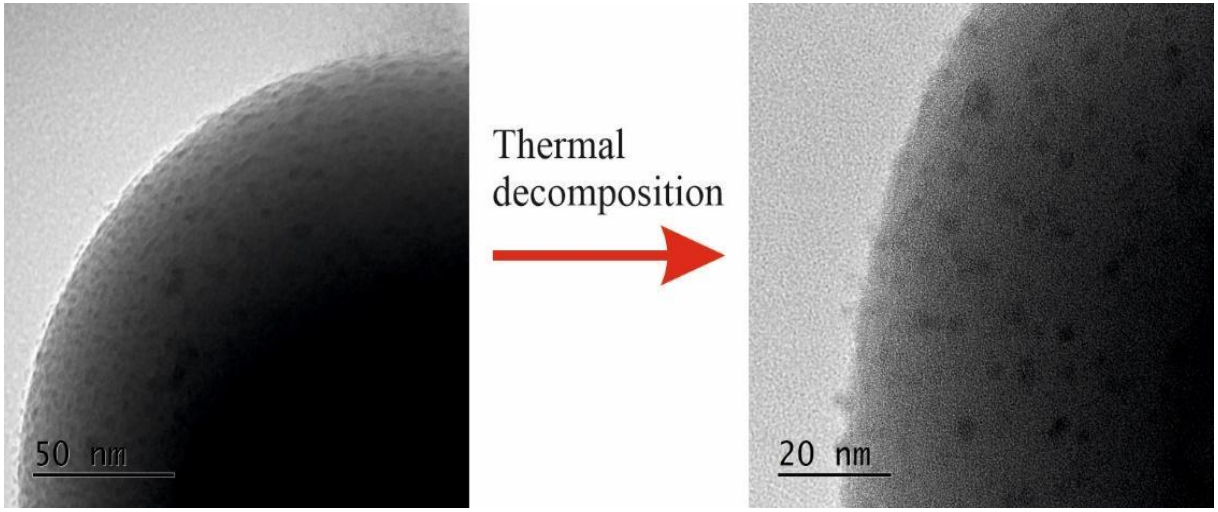


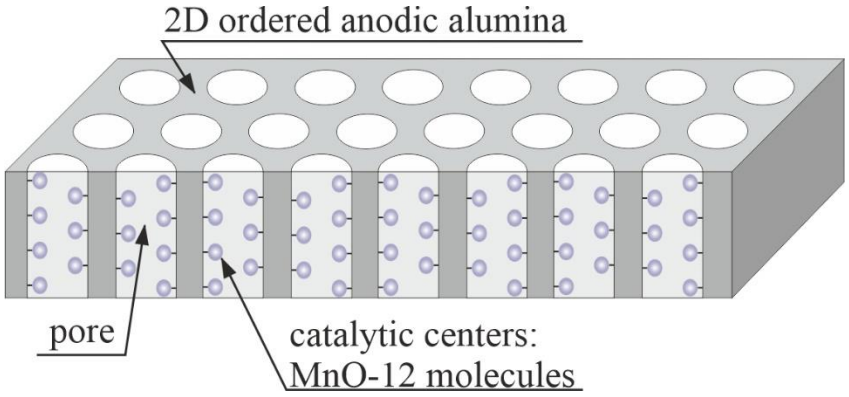
The value of energy barrier can be related with the structure of the anchored Mn_{12}-st molecules.
The observed differences in the energy barrier can be explained as a consequence of the deposition on the surface, which introduce the modification of axial anisotropy

Magnetic analysis confirms the possibility of functionalization of the surface by Mn_{12}-st SMMs with preservation of typical magnetic behaviour

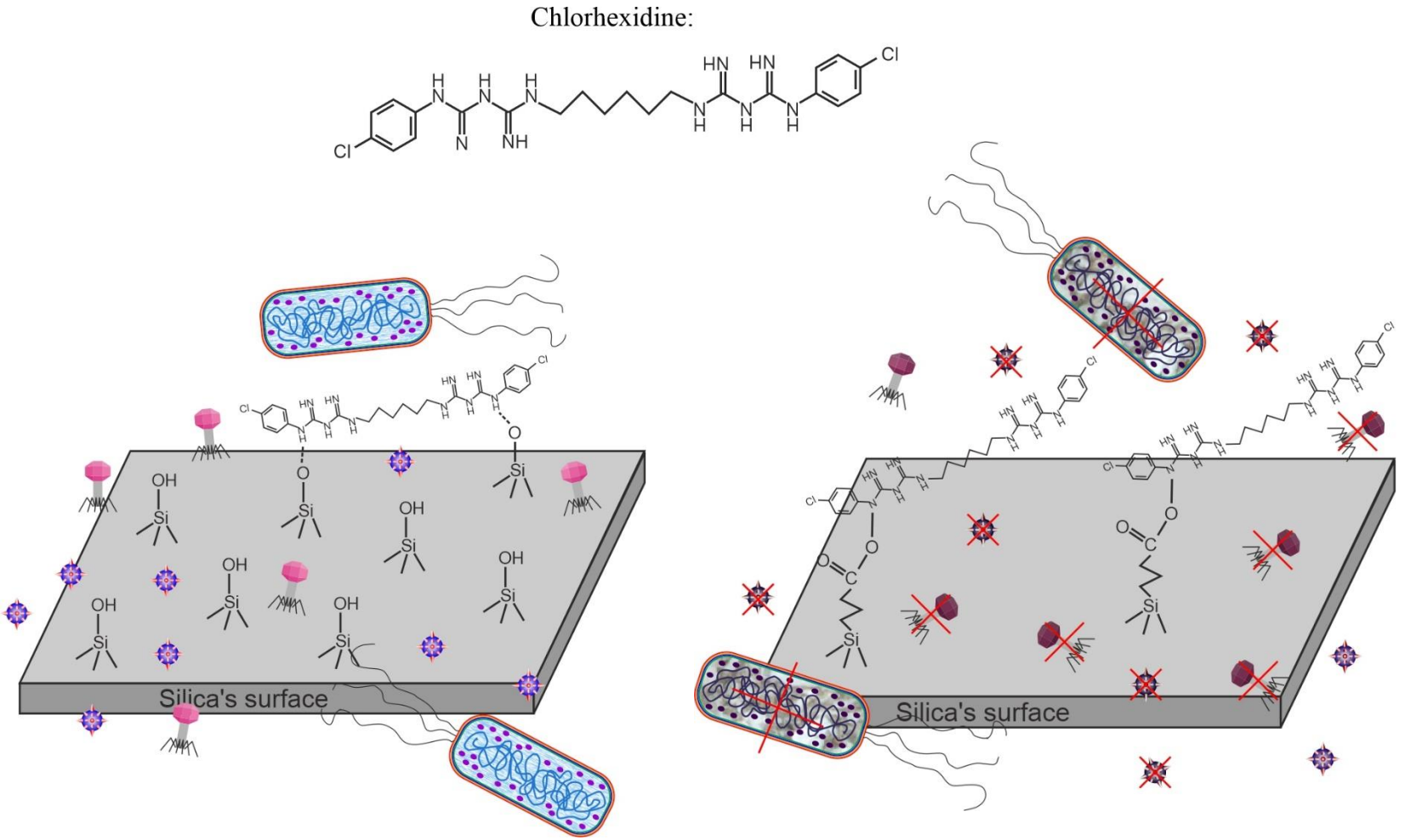
M. Laskowska, O. Pastukh, P. Konieczny, M. Dulski, M. Zalasiński and Ł. Laskowski: Magnetic behaviour of Mn_{12}-stearate single-molecule magnets immobilised on the surface of 300 nm spherical silica nanoparticles, Materials 13 (2020), 2624

A good starting point for nanocomposites

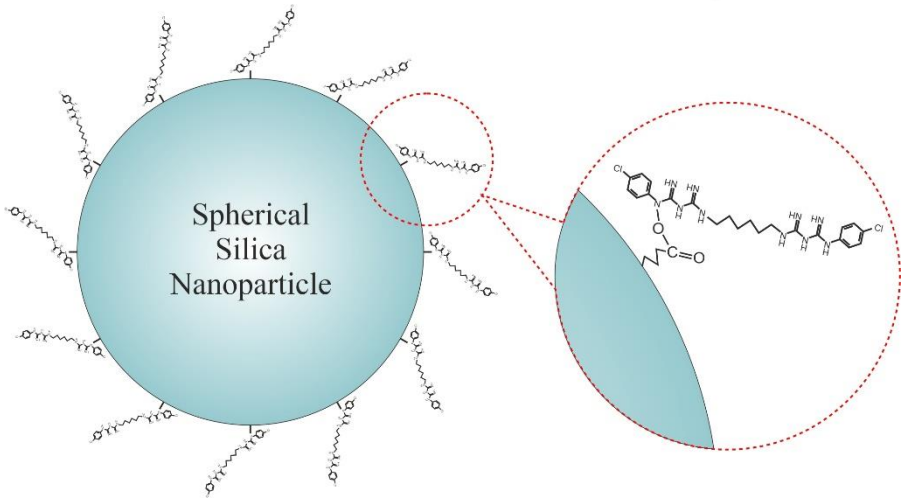




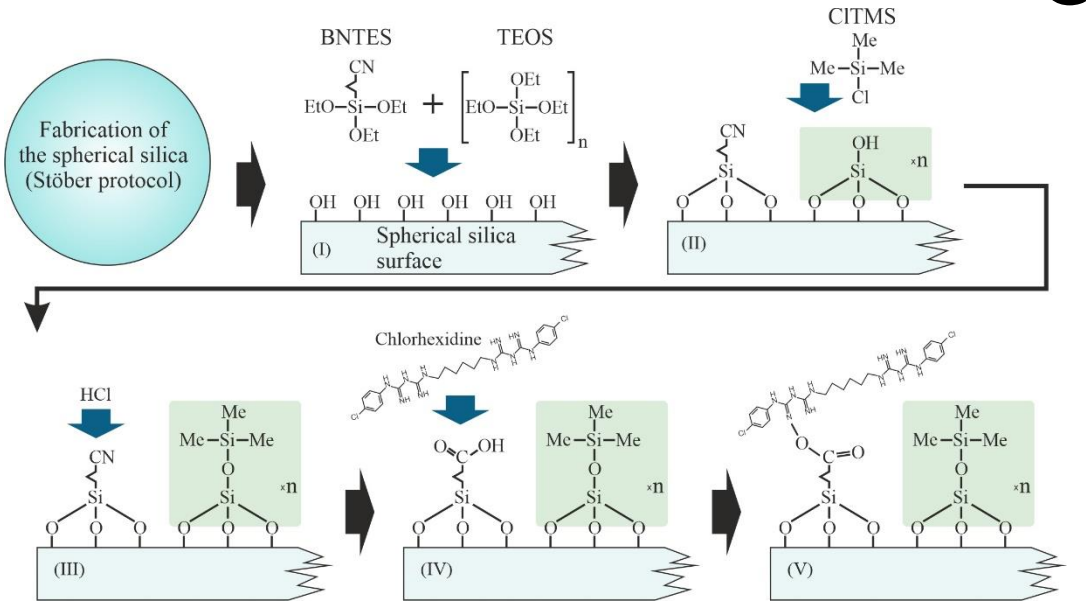
That's not all prospects for the spherical silica



Where is the spherical silica here?



B-STING:
Biocidal **S**ilica-
Templated
Immobilized **N**ano-
Groups



To sum up…

- All the presented materials were based on 2D solid solvent concept
- 2D solving in proper solids provides us with the possibility of preparation countless novel materials
- In the most cases the technology is robust and no need sophisticated methods

Acknowledgement

Dr Magdalena Laskowska

My team:

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- Andrii Fedorchuk
- Dr Anna Nowak
- Dr Dominika Kuźma
- Dr hab. Małgorzata Kąc
- Oleksandr Pastukh

My friends from other units:

- Prof. Iwan Kityk (Czestochowa University of Technology)
- Dr hab. Piotr Pawlik Prof. PCZ (Czestochowa University of Technology)
- Prof. Alain Walcarius (LCPME France)
- Dr Neus Vila (LCPME France)
- Prof. Munetaka Oyama (Kyoto University, Japan)
- Prof. Ali Umar (Kebangsaan University, Malesia)
- Dr Mateusz Dulski (University of Silesia)
- Dr Maciej Zubko (University of Silesia)

Than you for your attention!

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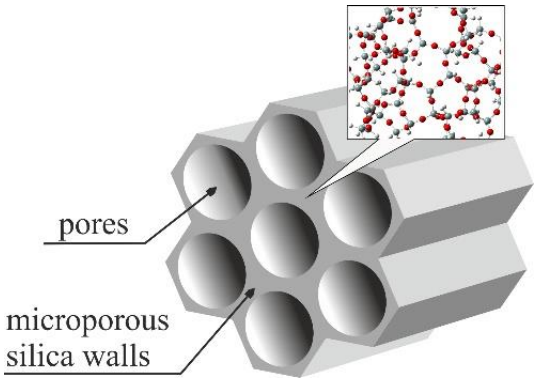
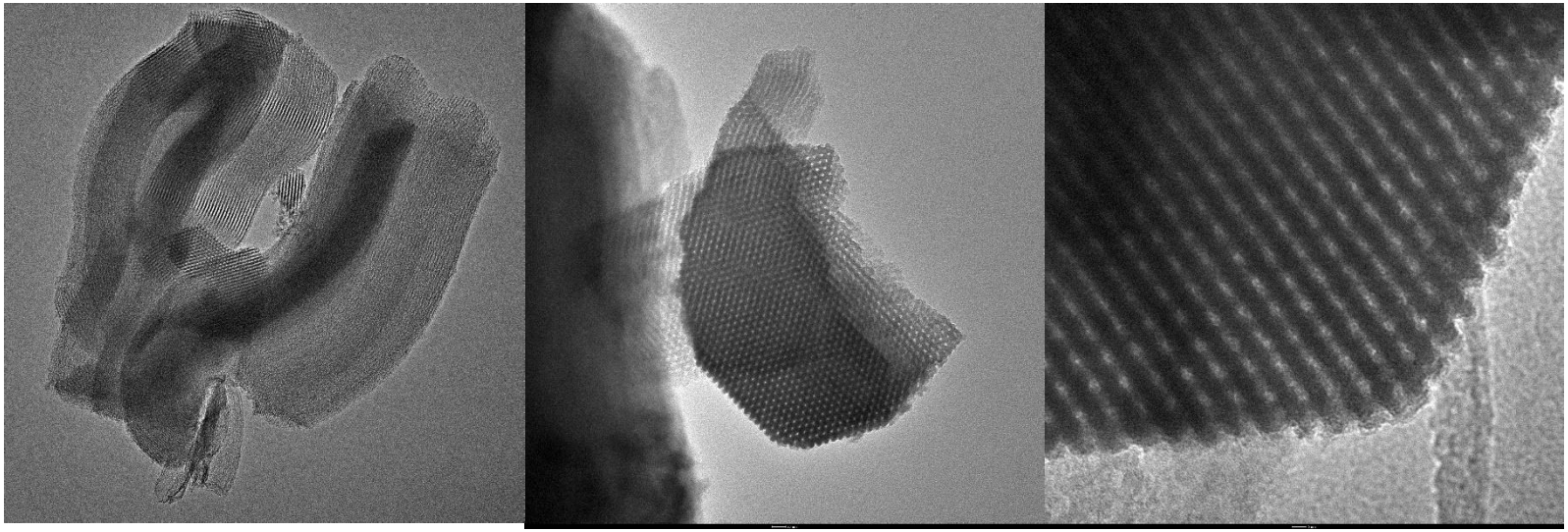
Materials for discussion

The material with the more developed surface

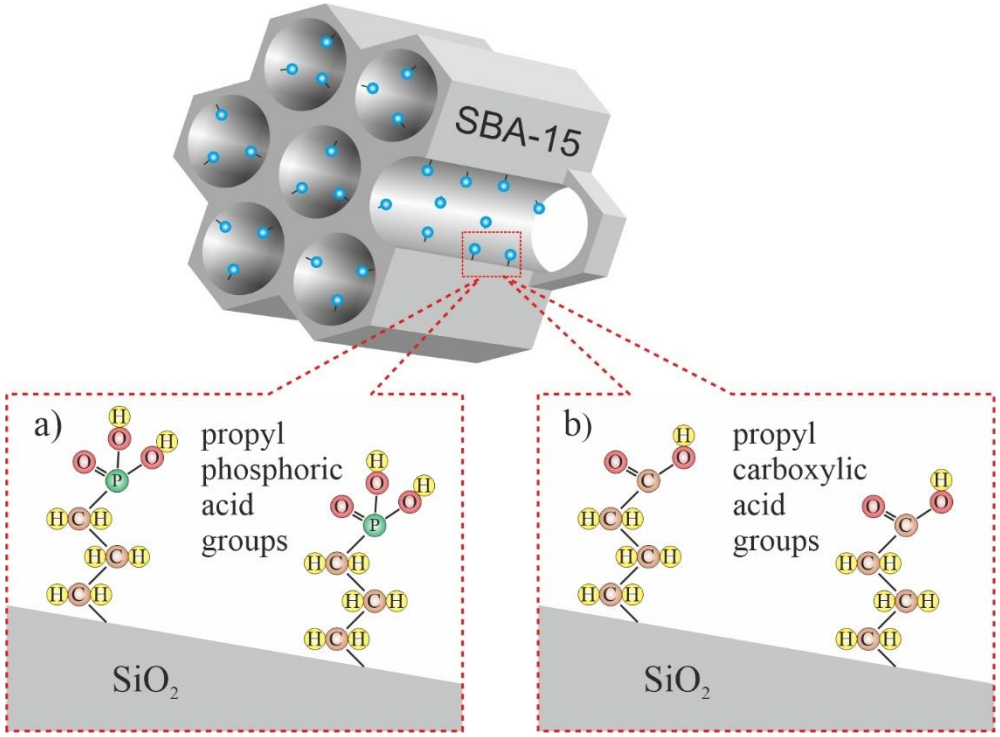


- Low-cost synthesis
- Non-toxic
- Highly uniform porosity
- Mechanical stiffness
- Thermal stability
- Hugh specific surface: over $700 m^2/g$

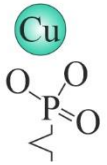


Ideal material as a matrix for 2D solid solvent: a wide possibilities of functionalization

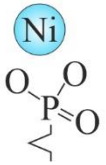
SBA-15: the prospectives for funtionalization



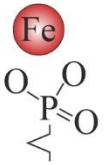
Silver carbonate



Copper phosphonate

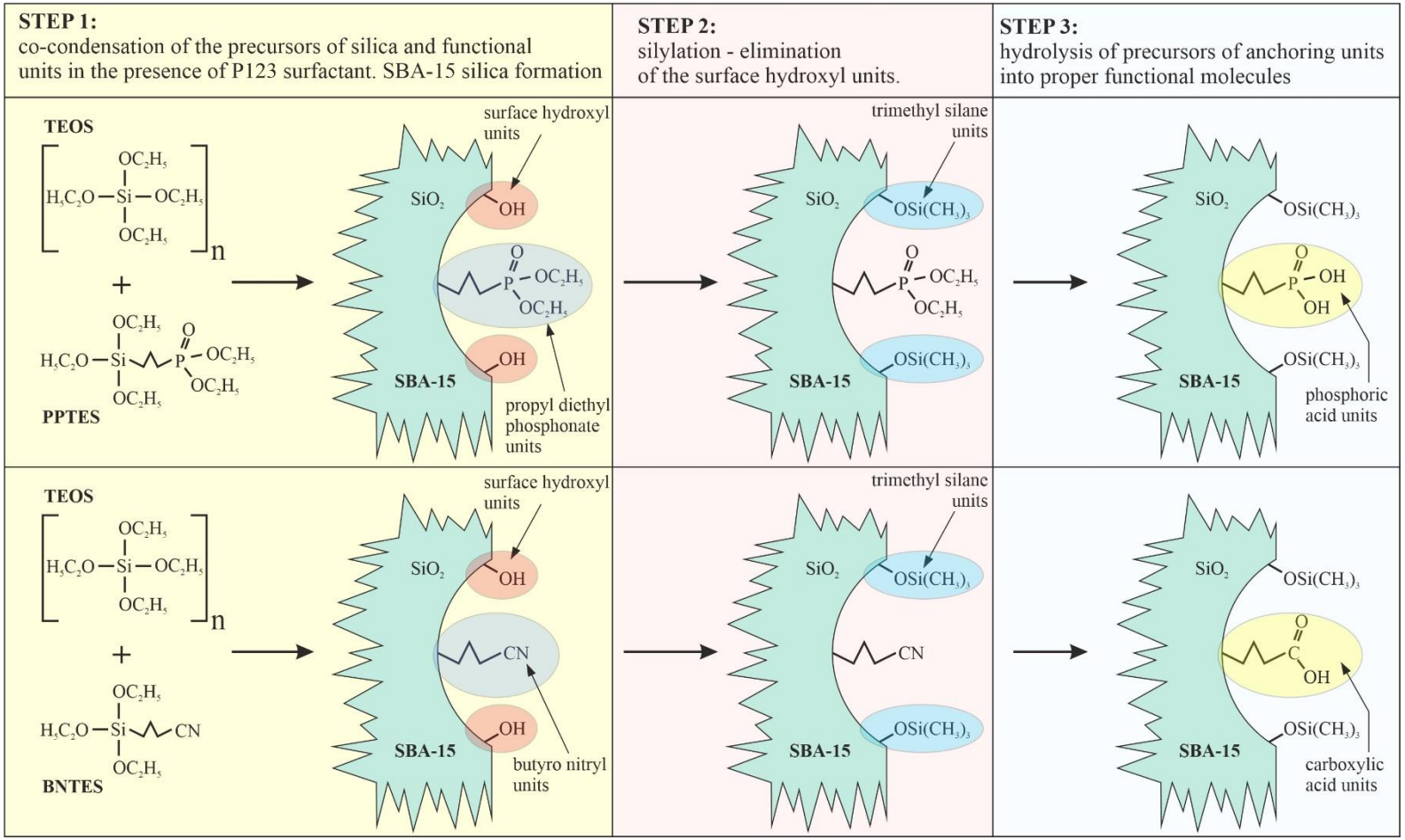


Nickel phosphonate



Iron phosphonate

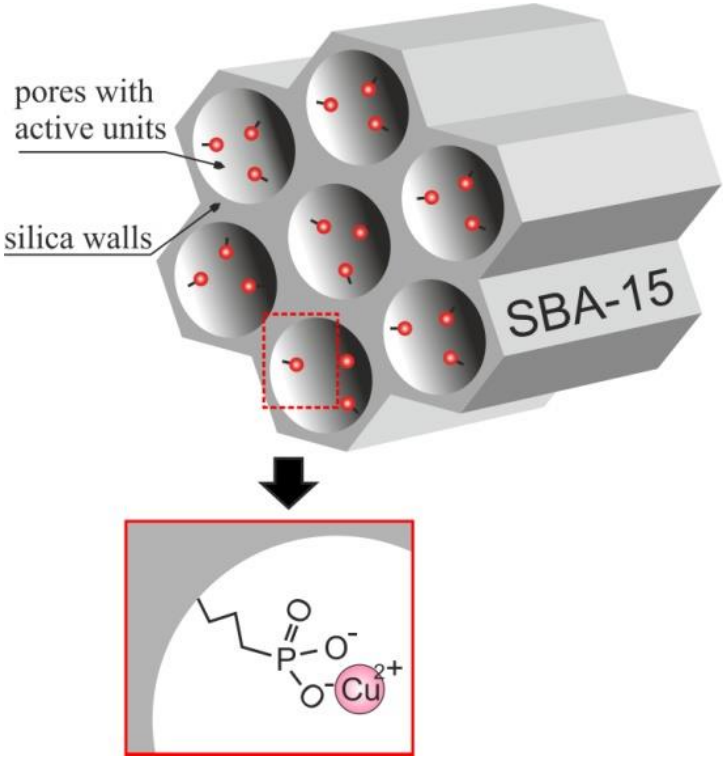
Functionalization procedure: co-condensation this time



Let's try dissolve copper ions

and make biocidal material

- Anchored active copper-containig units: limiting of migration into environment, limited depleting
- Silica matrix allows for using as a modifiers for polymers
- Silanation of the matrix: self-cleaning properties

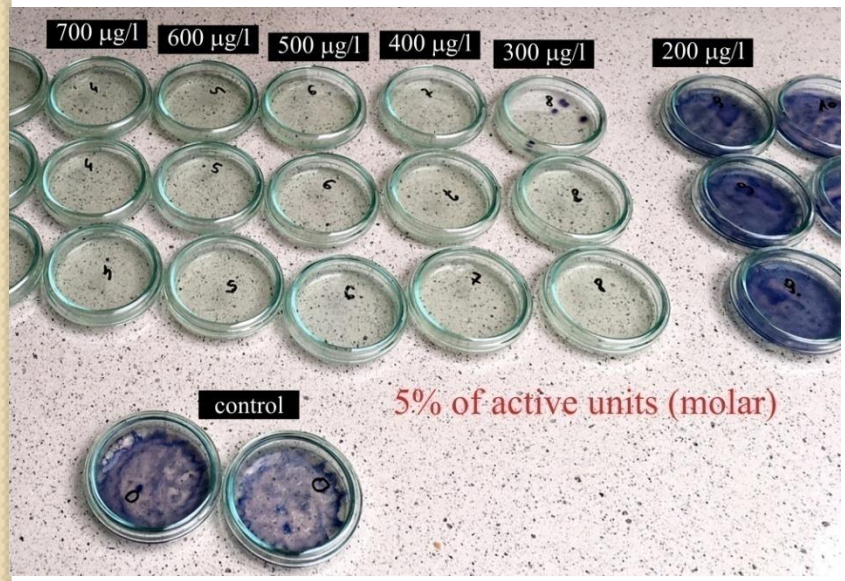


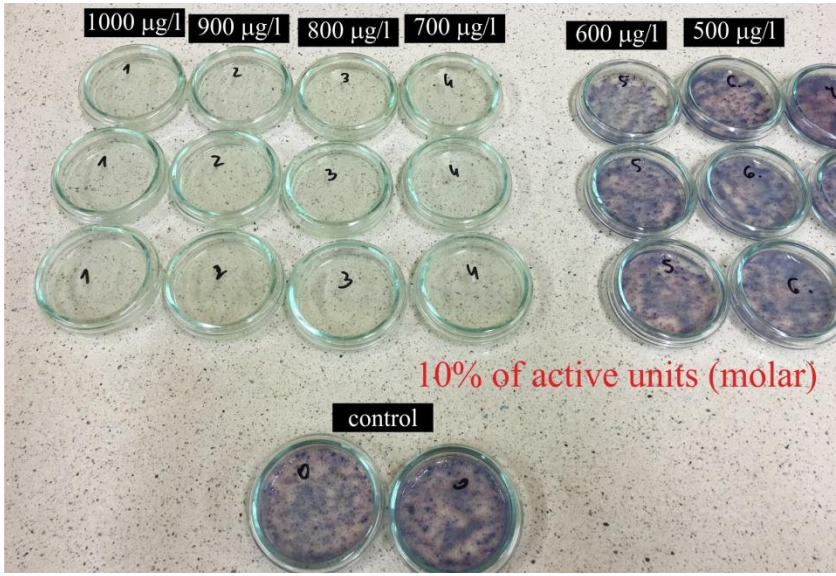
Łukasz Laskowski, Magdalena Laskowska: Functionalization of SBA-15 mesoporous silica by Cu-phosphonate units: probing of synthesis route, Journal of Solid State Chemistry, 220 (2014) 221–226

Does it works?

Strange antimicrobial action…

bactericidal activity (*e-coli*) increase with the decreasing of functional groups concentration

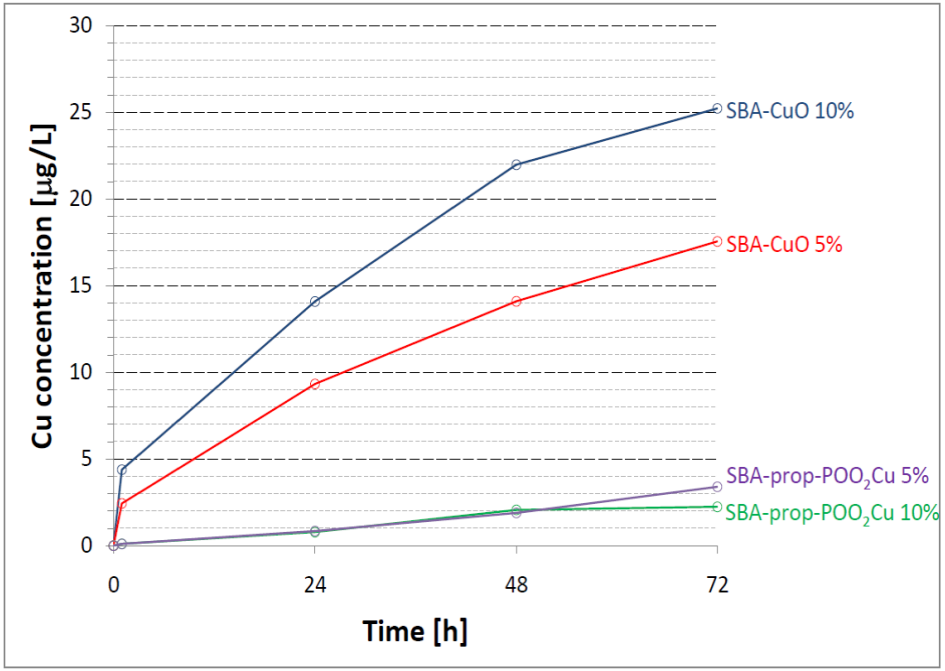




Łukasz Laskowski, Magdalena Laskowska, Krzysztof Fijałkowski, Henryk Piech, Jerzy Jelonkiewicz, Marta Jaskulak, Adam Gnatowski, Mateusz Dulski: New class of antimicrobial agents - SBA-15 silica containing anchored copper ions, Journal of Nanomaterials (2017) 1287698

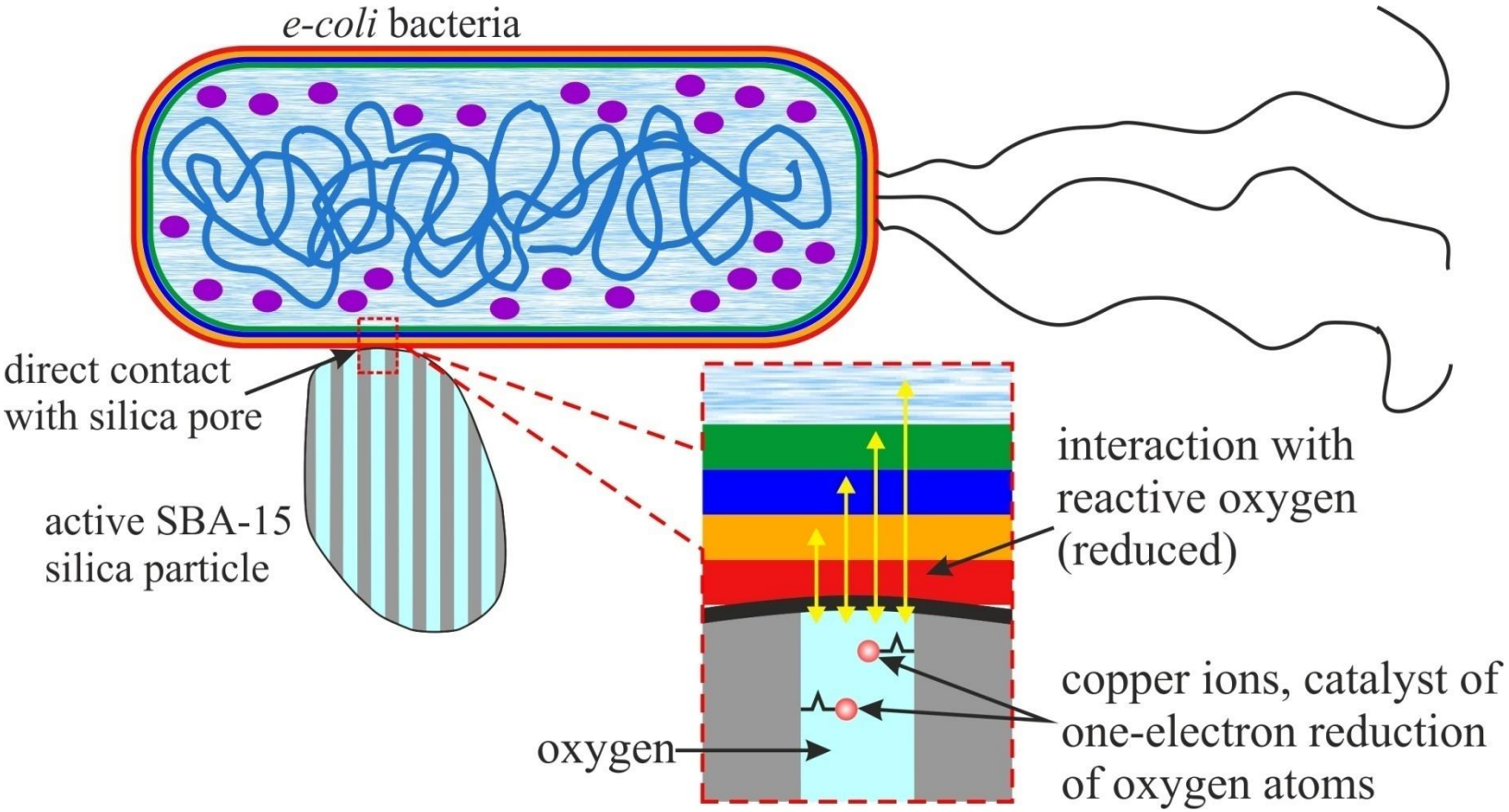
Let's solve the puzzle

- Oxygen content: elemental analysis (Vario EL cube + pyrolysis attachment)
- Copper ions mobility: atomic absorption spectroscopy (Shimadzu model AA-680)

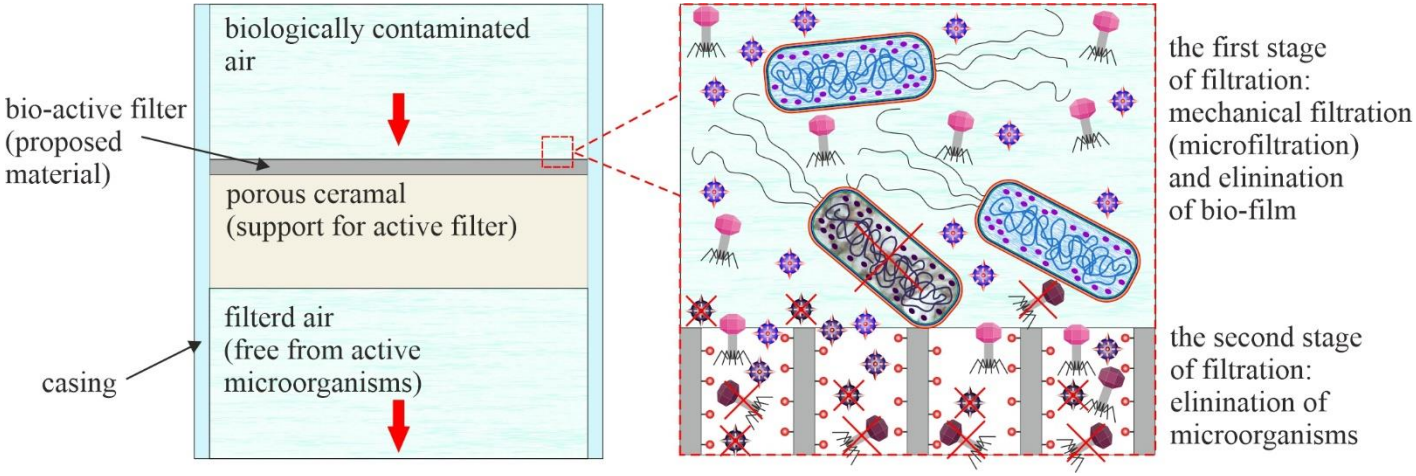


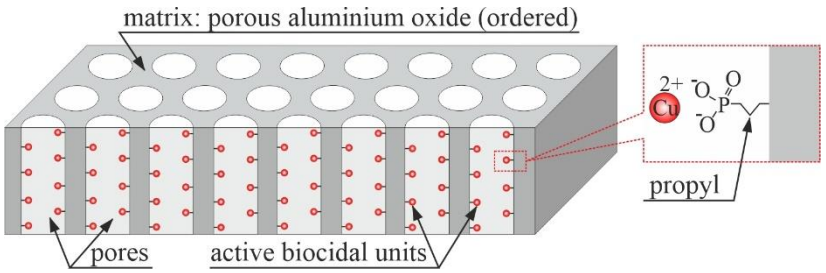
Specimen	Oxygen percentage content [%]:	
	Theoretical value	Elemental analysis result
SBA-prop-$PO(OH)_2$ 5%	51.35	52.04
SBA-prop-$PO(OH)_2$ 10%	49.72	51.39
SBA- CuO 5%	52.45	56.32
SBA- CuO 10%	51.74	57.01
SBA-prop-POO_2Cu 5%	49.04	**77.32**
SBA-prop-POO_2Cu 10%	45.75	**69.21**

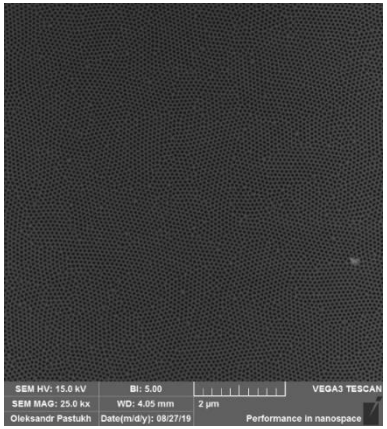
It's not active units killed bacteria…

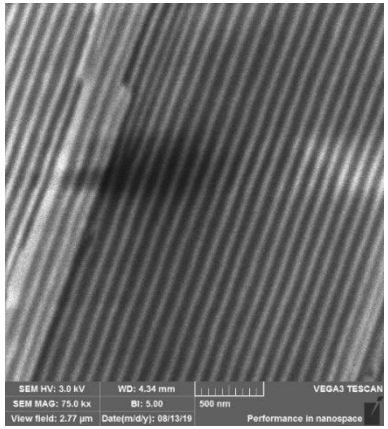


We have a unique antimicrobial system, what's next?



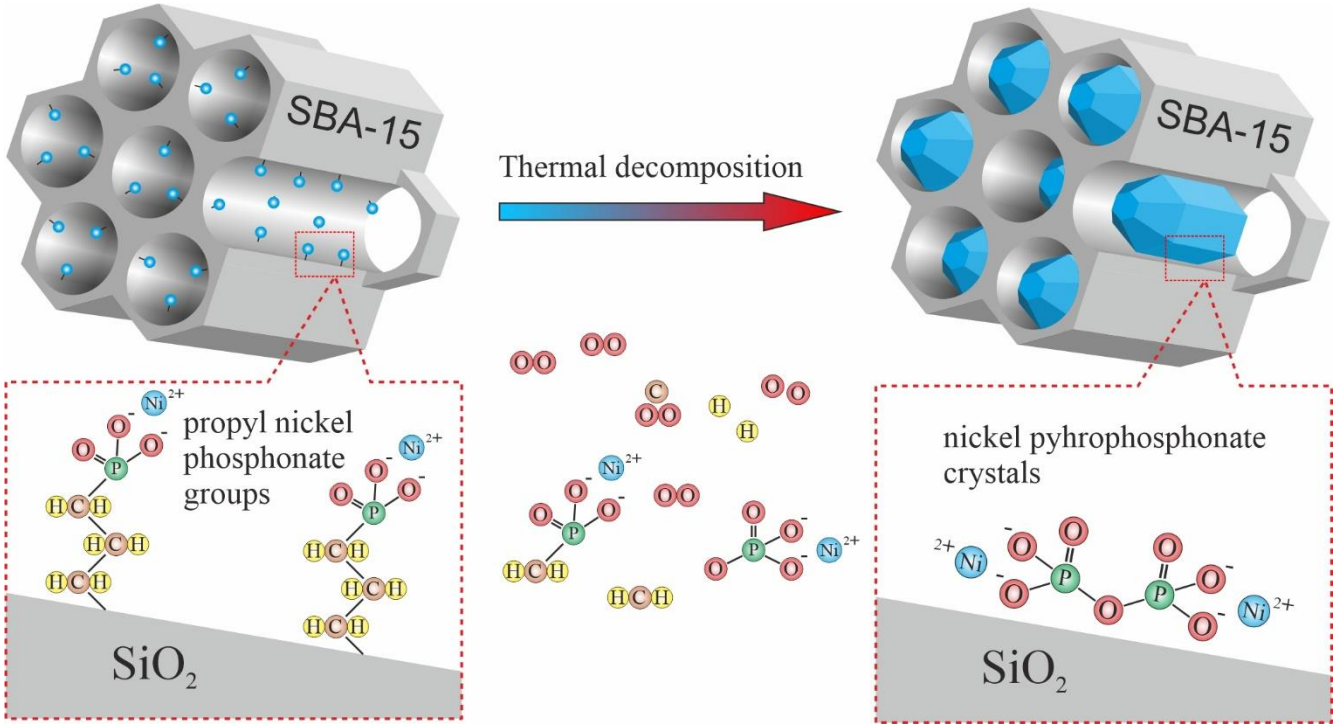




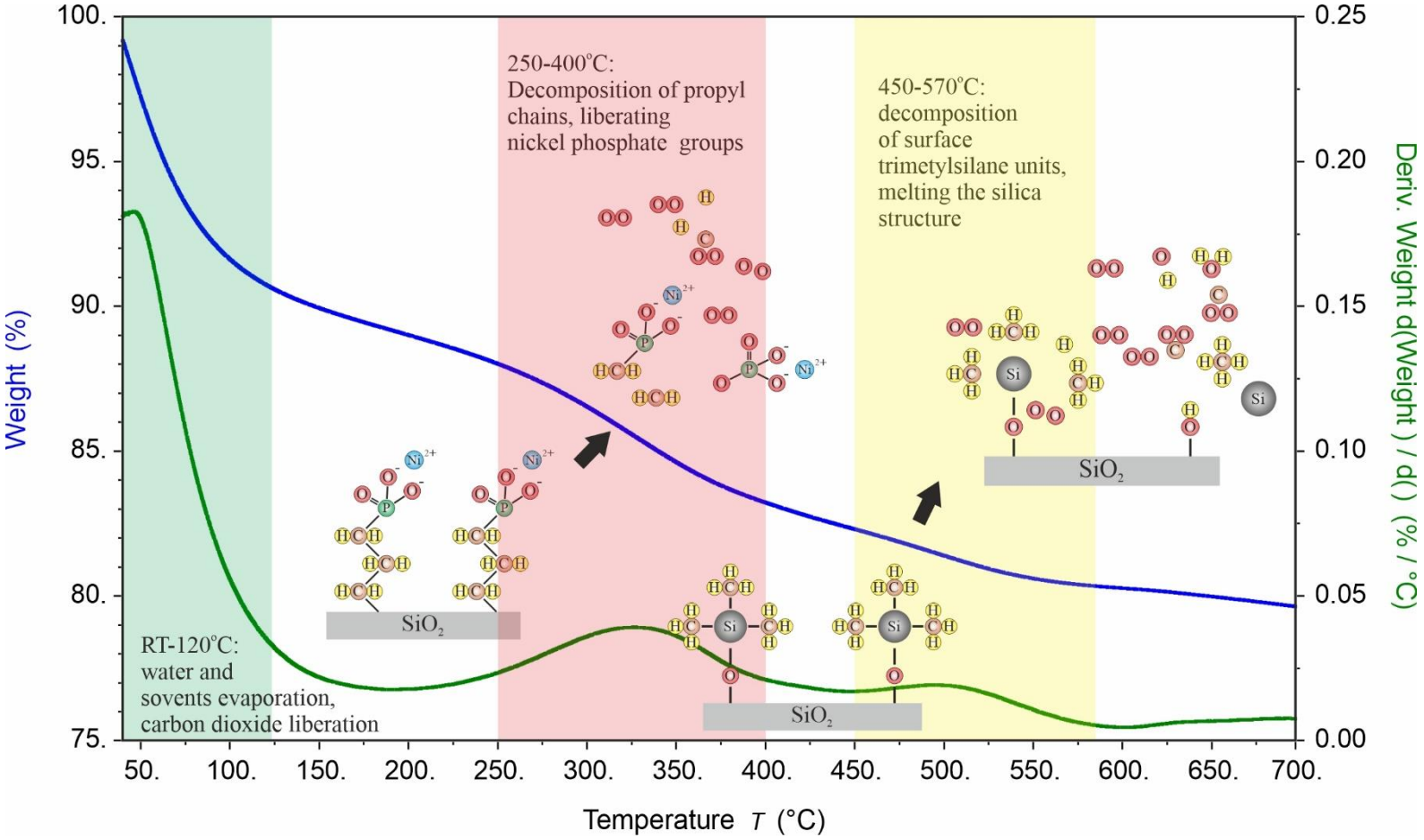


SBA-15 silica with metal ions: a starting point for novel materials

- Pores in functionalized silica can be treated as **silica nanoreactors**:
  - By selecting the appropriate functional units, we can play with the atomic composition of the "reagents" inside nanoreactor,
  - Modifying the doping rate enables the number of reagents to be set.
  - This results in obtaining the desired compounds with desired sizes precisely inside the silica pores.

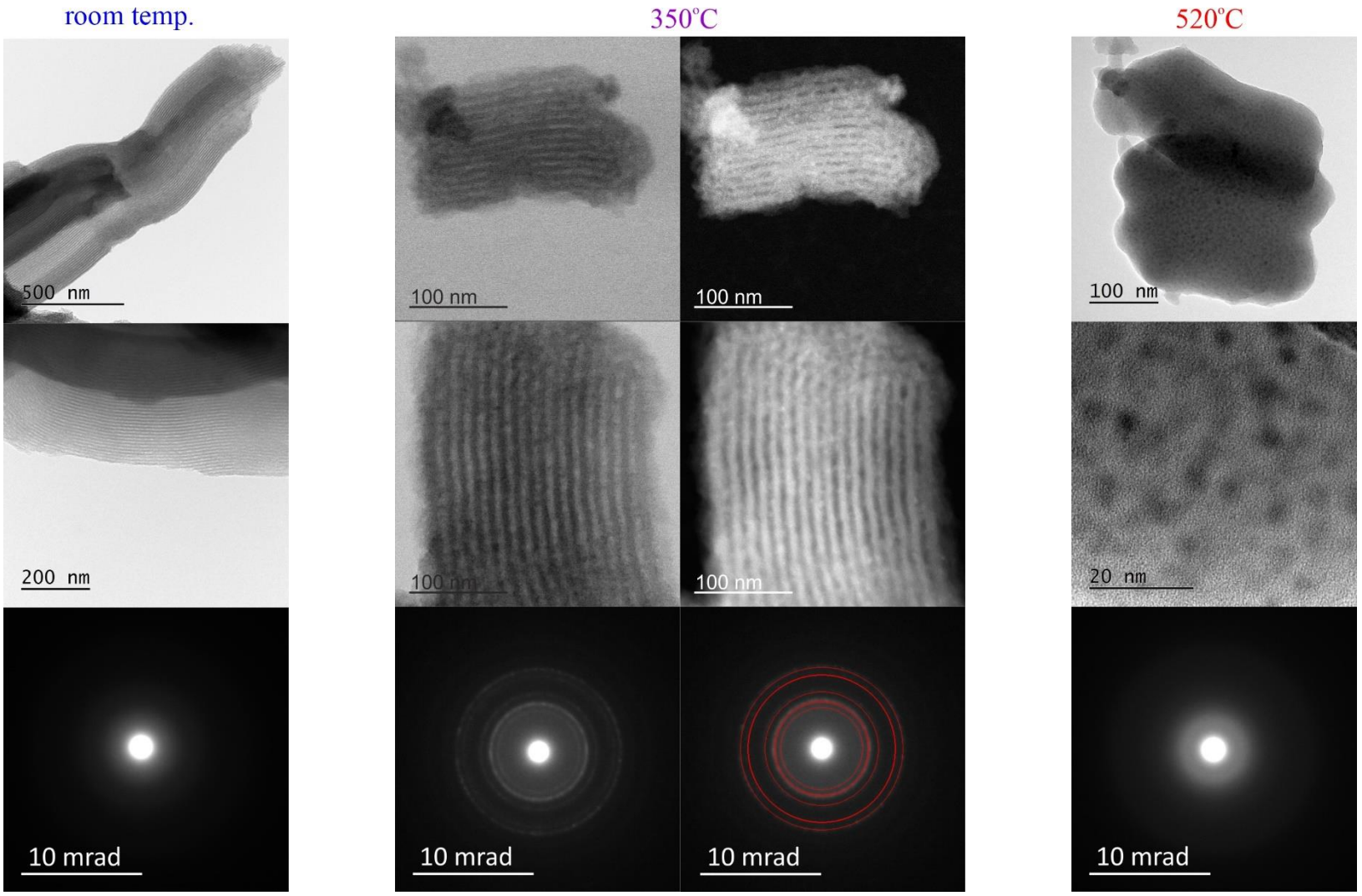


How to find the parameters?

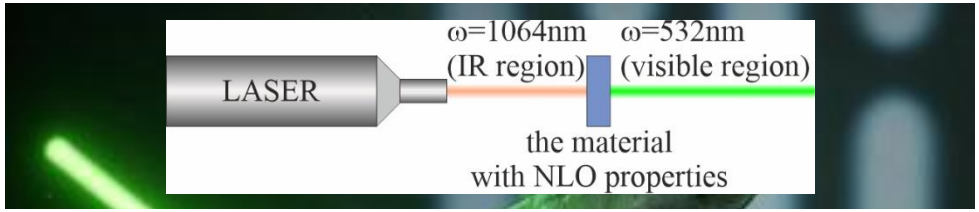


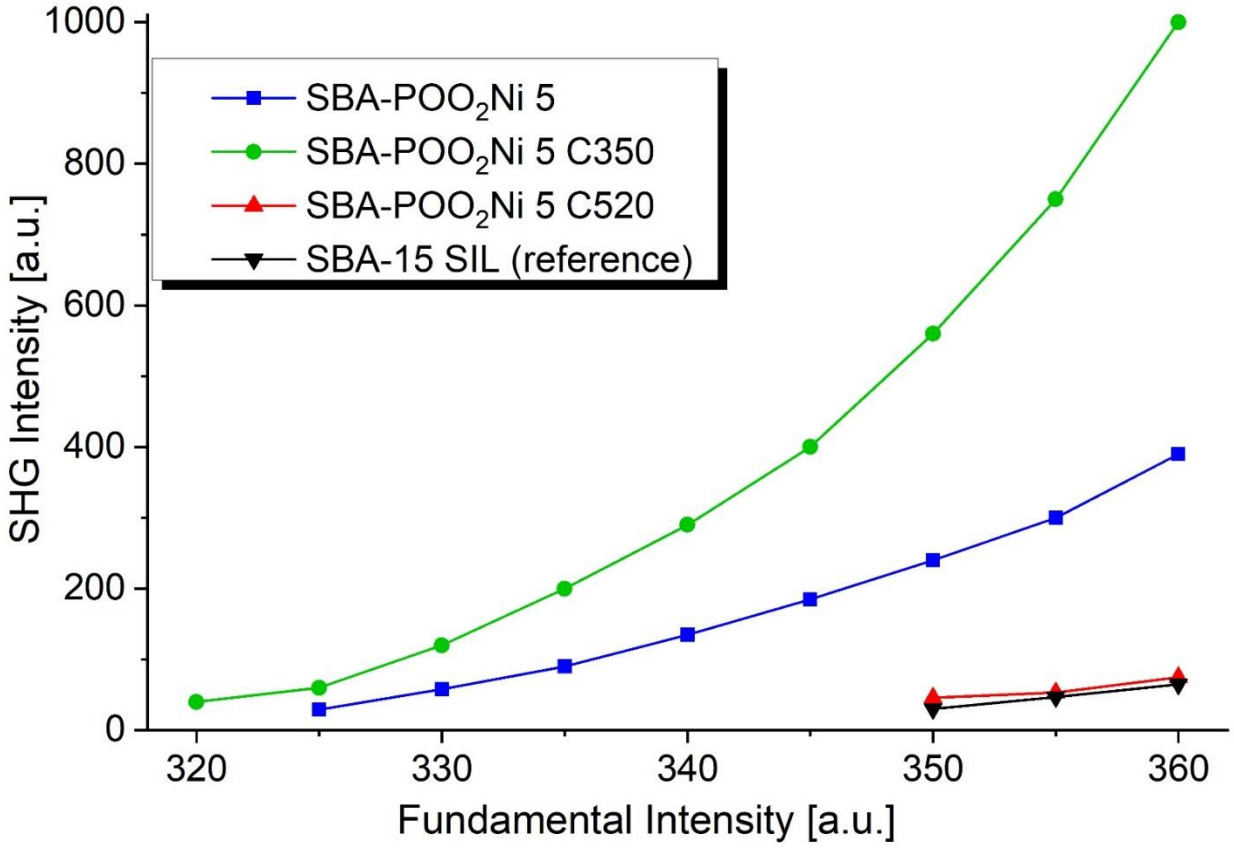
M. Laskowska, I. Kityk, O. Pastukh, M. Dulski, M. Zubko, J. Jedryka, K. Cpałka, P. M. Zielinski and Ł Laskowski, Nanocomposite for photonics - nickel pyrophosphate nanocrystals synthesised in silica nanoreactors, Microporous and Mesoporous Materials, 306 (2020), 110435

Do the silica nanoreactors works?

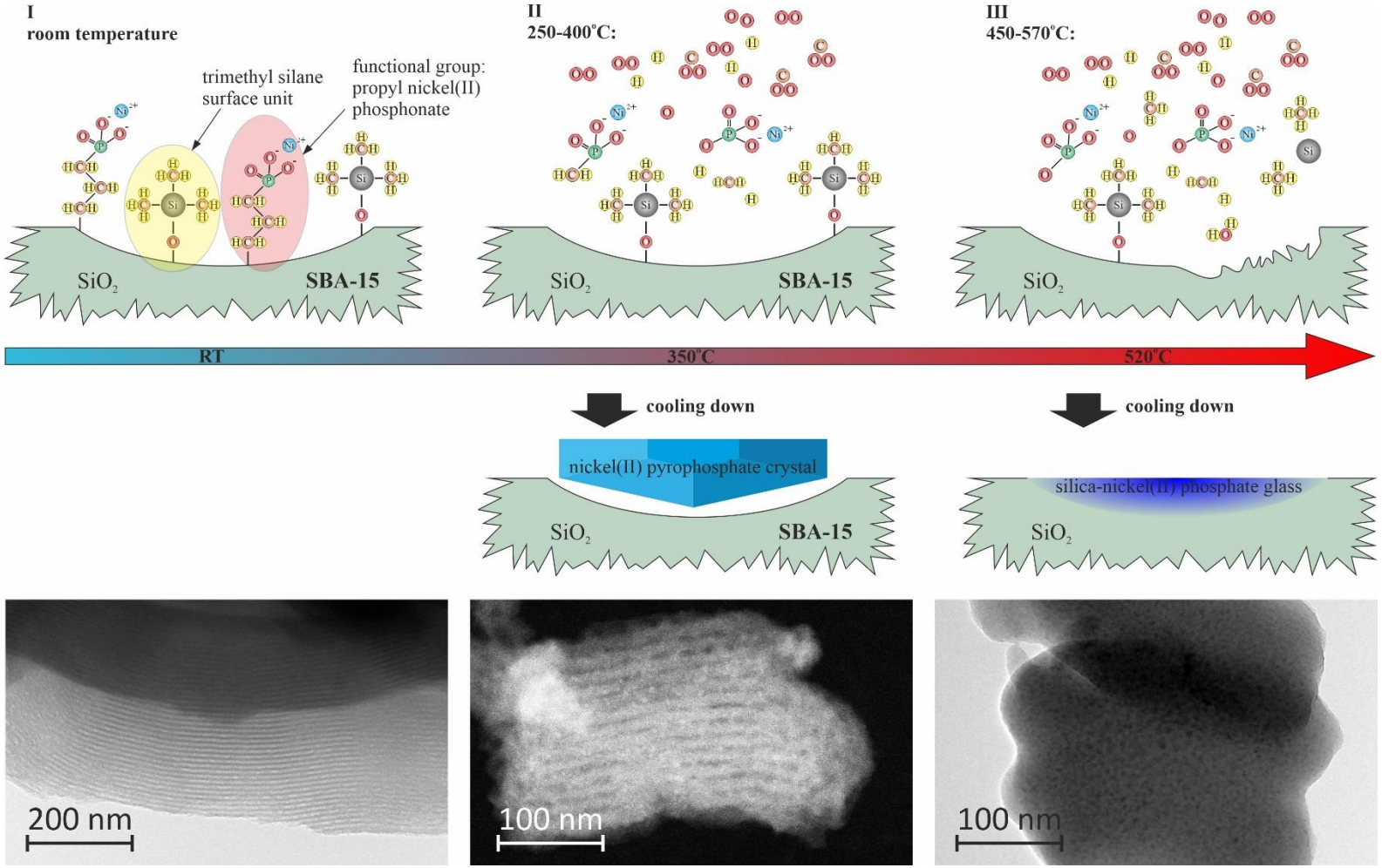


The material was fabricated purposely… for photonics

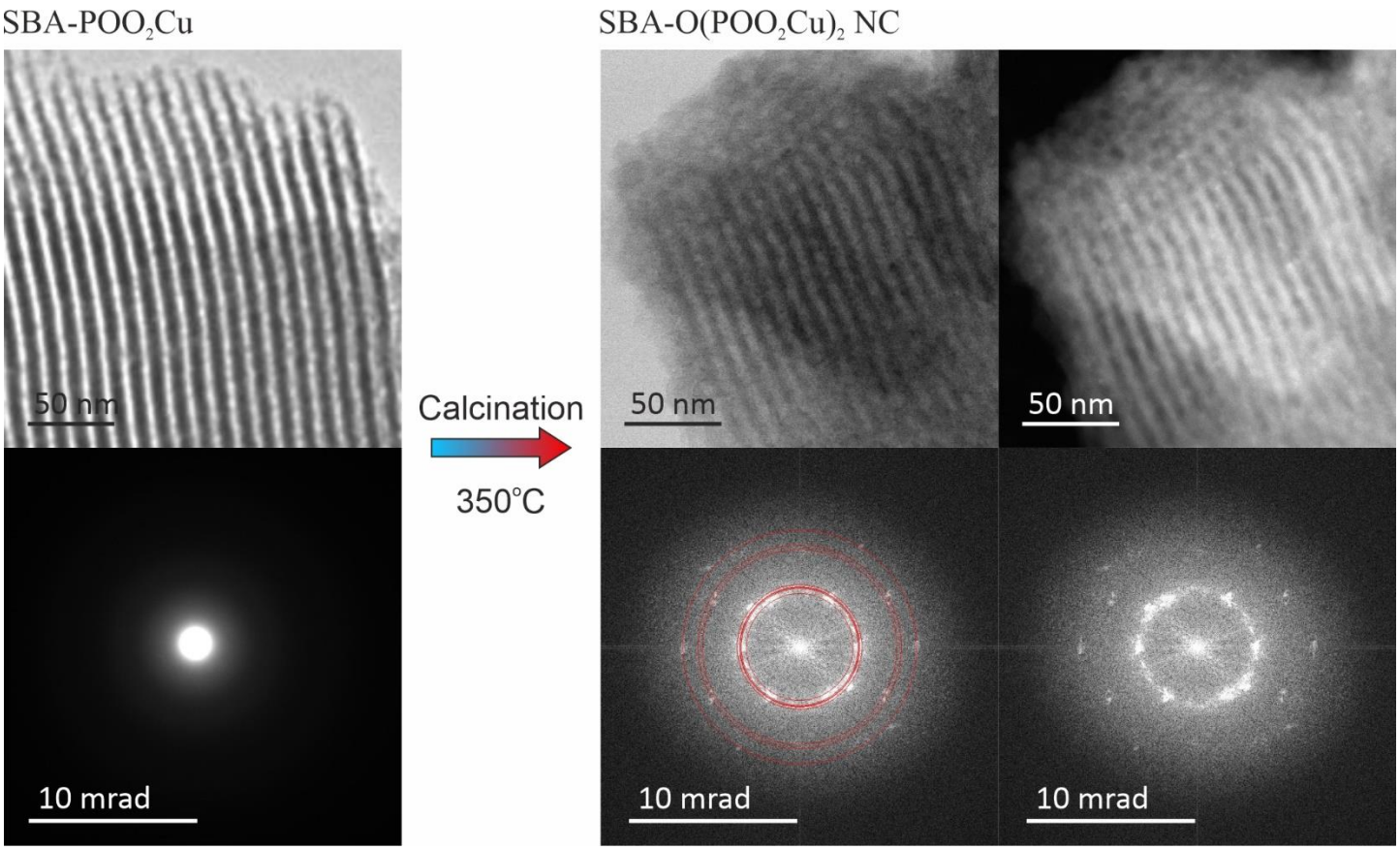




Now we know, what really happens with the material with heating

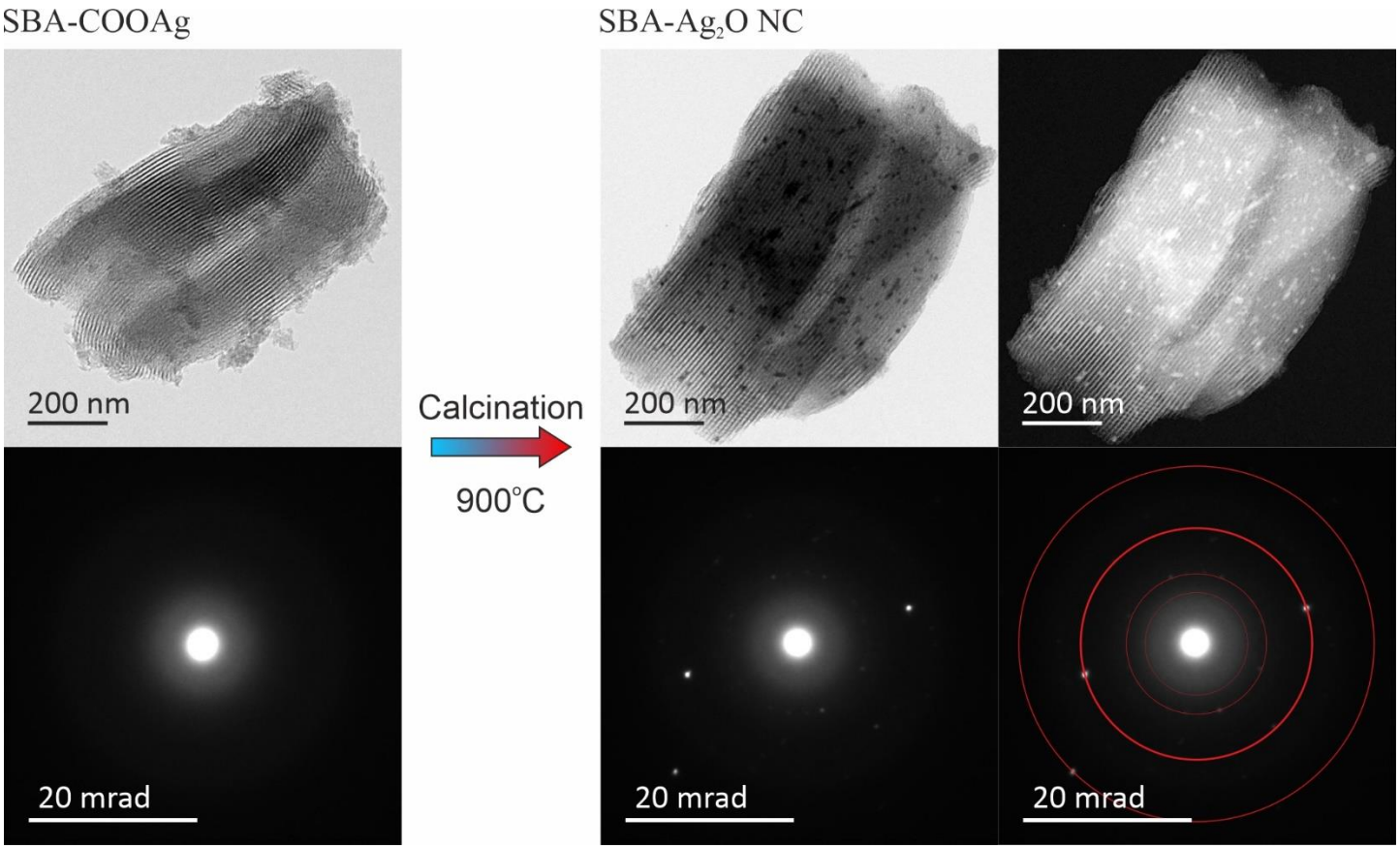


The idea of silica nanoreactors for another functional units: copper



L. Laskowski, A. Majtyka-Piłat, K. Cpałka, M. Zubko and M. Laskowska, Synthesis in silica nanoreactor: copper pyrophosphate quantum dots and silver oxide nanocrystallites inside silica mezochannels, Materials 13 (2020) , 2009

And something similar with silver



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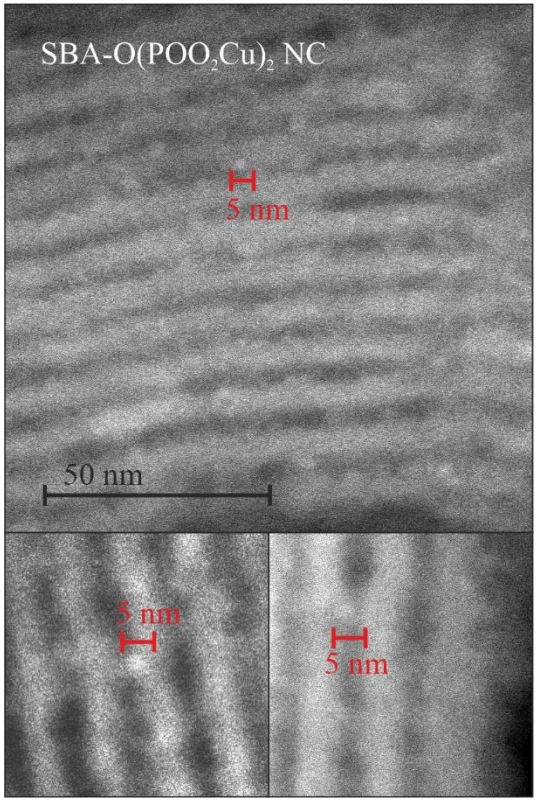
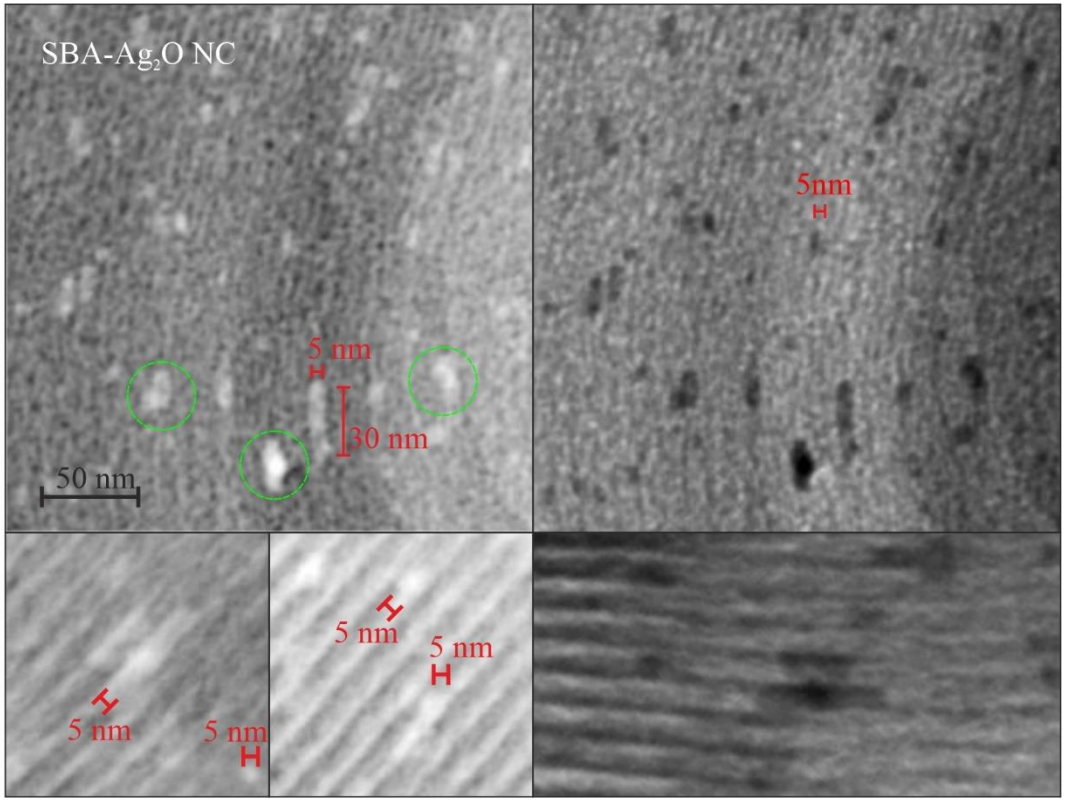
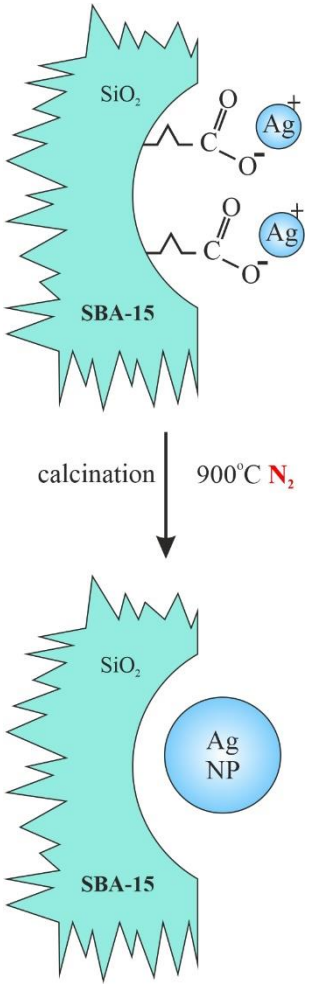
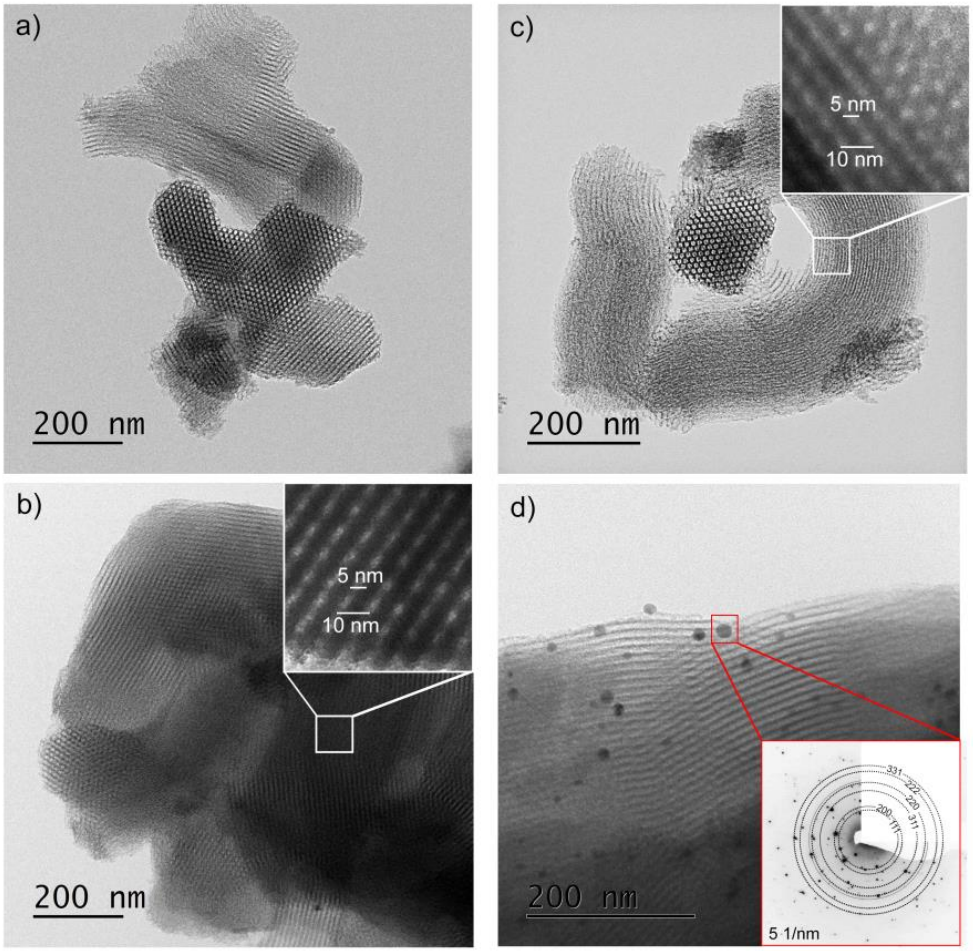
Note the sizes of crystals





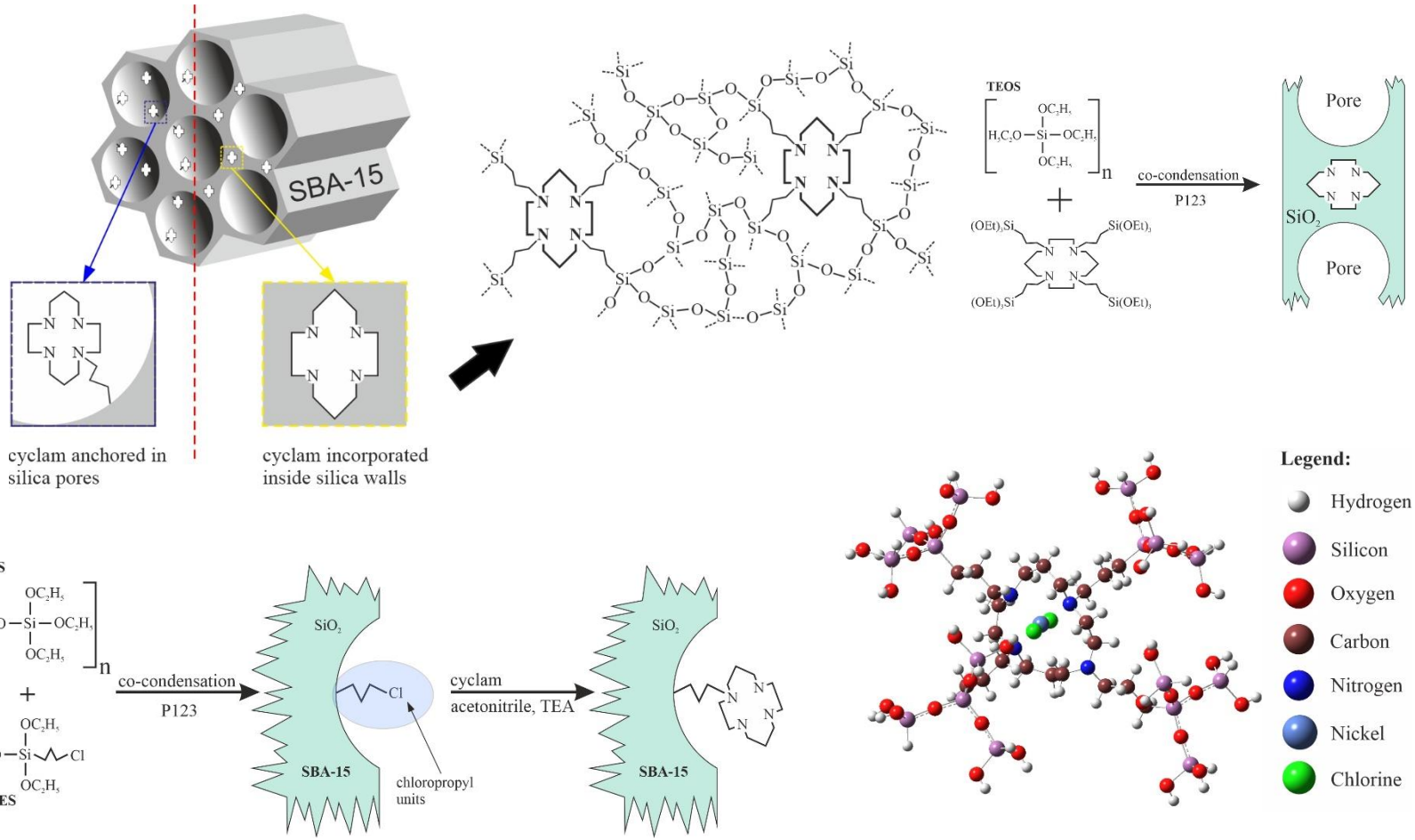
The calcination conditions matter!





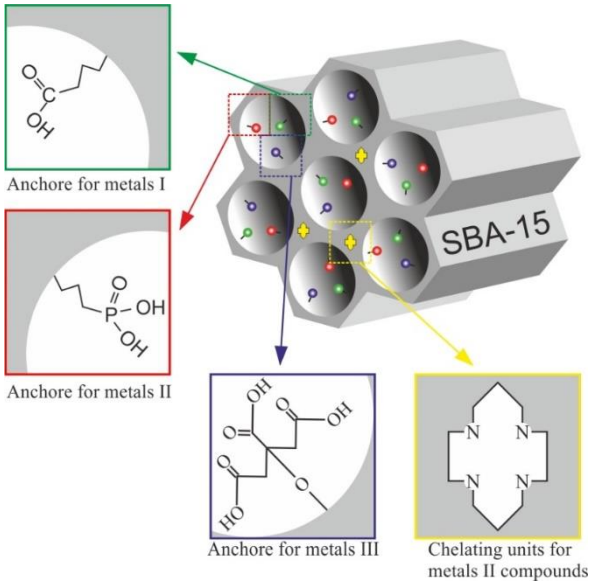
M. Dulski, M. Laskowska, S. Sułowicz, T. Krzykawski, , P. M. Zielinski , P. Pawlik. O. Pastukh, A. Nowak and Ł. Laskowski, Impact of silica mesopores functionalization on structural and biological features of SBA-15, Microporous and Mesoporous Materials

Functionl units inside pores… it's not enough!

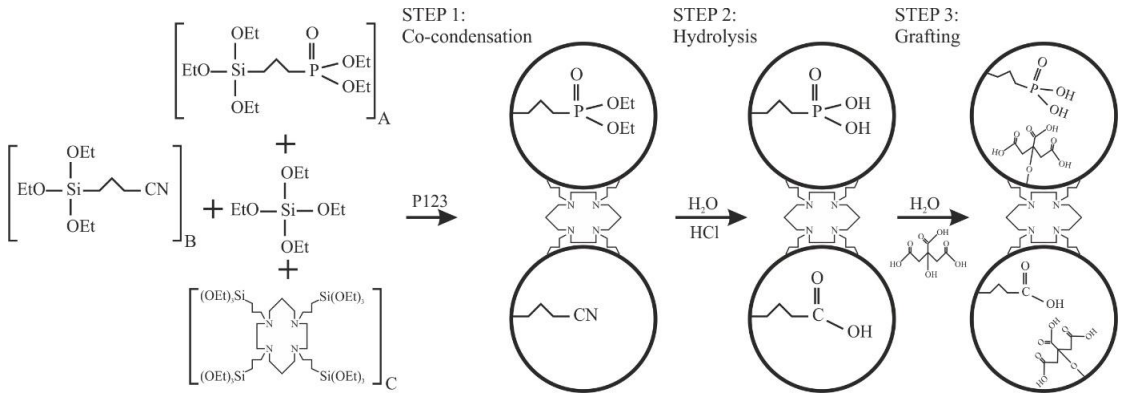


M. Laskowska, M. Dulski, M. Marszałek, M. Zubko, Ł. Laskowski*, Vertically aligned porous silica thin films functionalized by nickel chloride incorporated in walls, Microporous and Mesoporous Materials, 276 (2019) 201-206

Having pores and walls to disposal, let's use it! For our environment



- The material for remediation of groundwater and soli
- Can be pressed into a pellet (cartridge) and used as it
- Capture various metals: Cu, Ag, Cd, Zn, Fe, Hg
- Insoluble: can be removed from the environment and substitute for a new one



- Highly applicative concept
- The interactions between precursors have to be checked

To sum up…

- The presented materials were based on 2D solid solvent concept
- 2D solving in proper solids provides us with the possibility of preparation countless novel materials
- In the most cases the technology is robust and no need sophisticated methods

Acknowledgement

Dr Magdalena Laskowska

My team:

- Dr Mateusz Schabikowski
- Andrii Fedorchuk
- Dr Anna Nowak
- Dr Dominika Kuźma
- Dr hab. Małgorzata Kąc
- Oleksandr Pastukh

My friends from other units:

- Prof. Iwan Kityk (Czestochowa University of Technology)
- Dr hab. Piotr Pawlik Prof. PCZ (Czestochowa University of Technology)
- Prof. Alain Walcarius (LCPME France)
- Dr Neus Vila (LCPME France)
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