

METROLOGICAL APPROACH TO SERS 3D PLATFORM CHARACTERISATION

Eleonora Cara
Advanced Materials and Life Science
INRiM

It-fab
Italian Network for
Micro and Nano Fabrication



METROLOGY

Metrology is the “science of measurement, embracing both experimental and theoretical determinations at any level of uncertainty in **any field of science and technology**” - BIPM



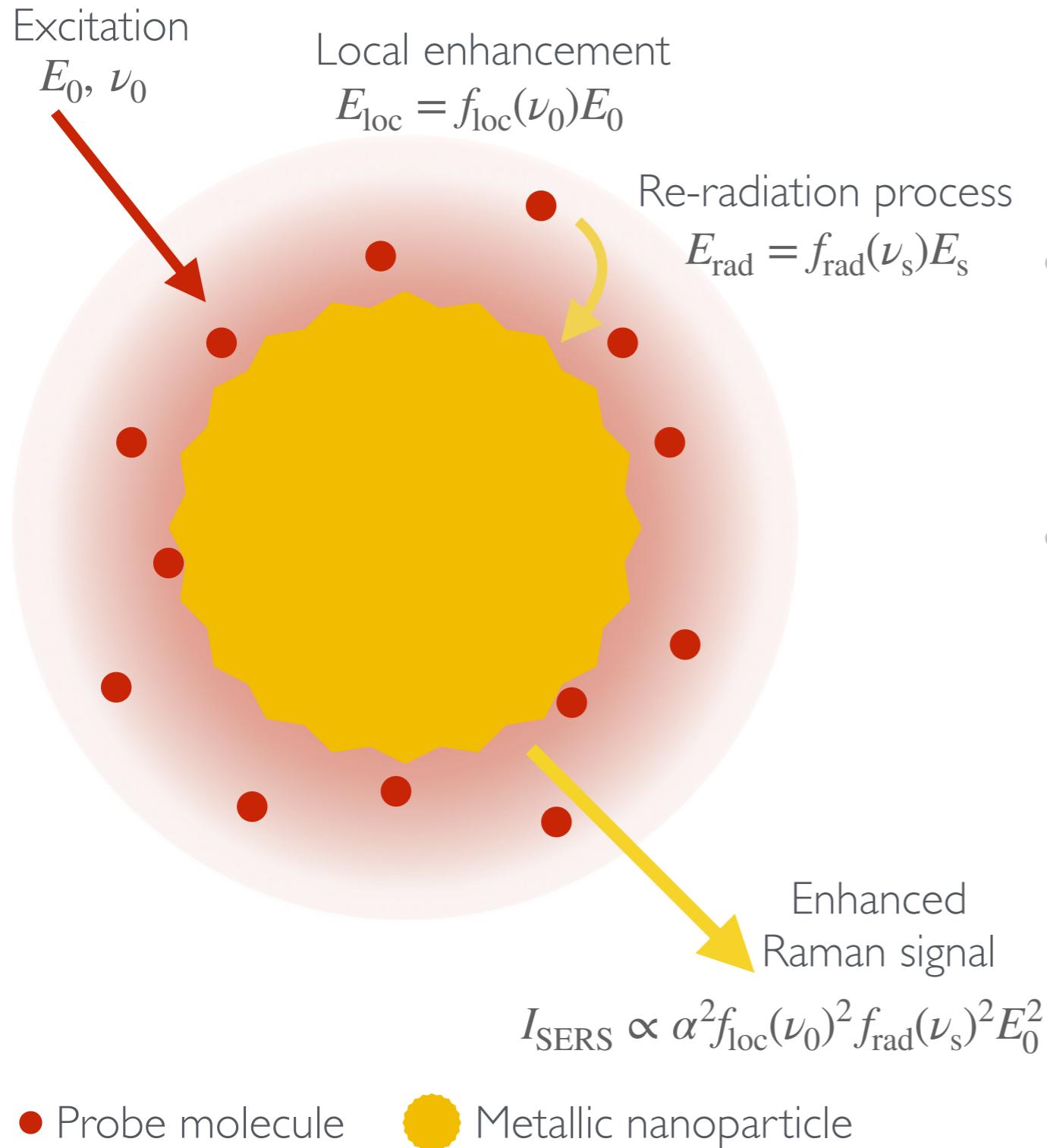
and more...

Important goals of metrology:
develop physical and chemical **analytical methods**
and promote the **comparison** of results

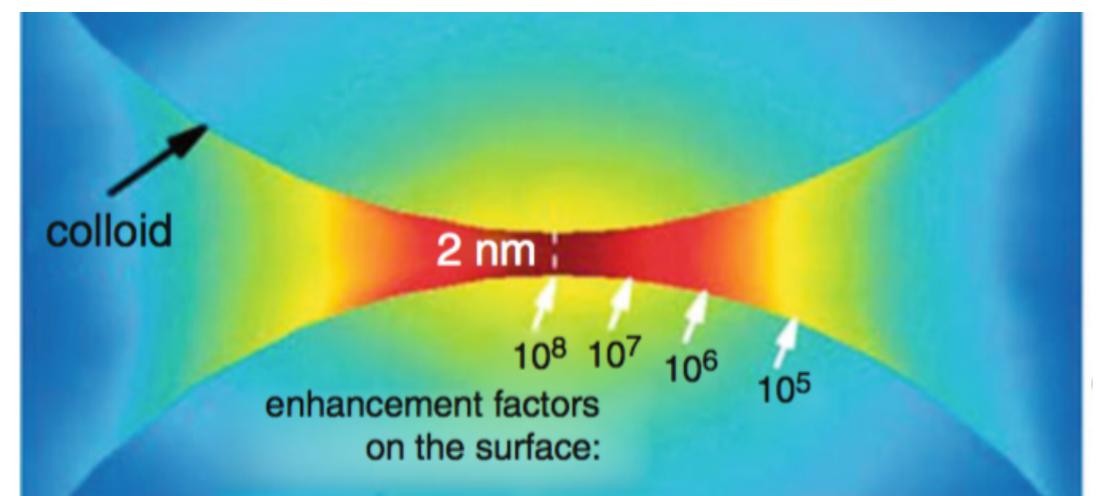
Surface-enhancement Raman spectroscopy (SERS)

1. Efficient **fabrication** for **active substrates**
2. Accurate evaluation of the **SERS performance**

SURFACE-ENHANCED RAMAN SCATTERING

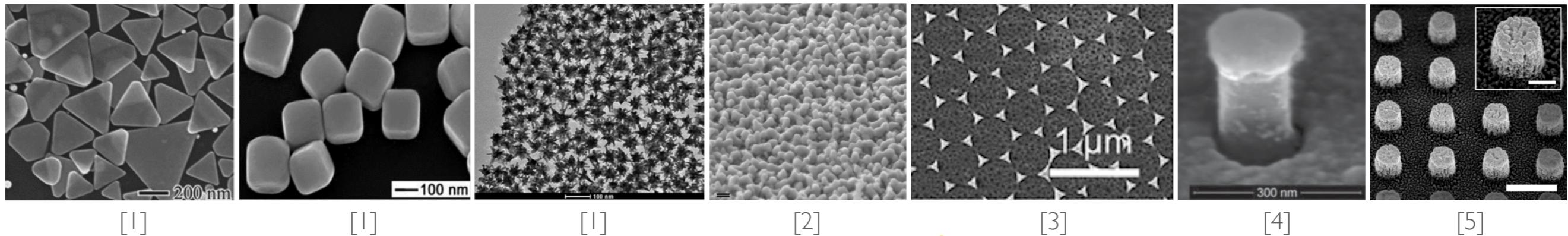


- Molecular fingerprint
- Two enhancement effects: chemical and electromagnetic
- Significant role of morphology: **hot spots**



Etchegoin, PG, Le Ru EC. Phys Chem Chem Phys, 2008, 10, 40

SERS SUBSTRATE

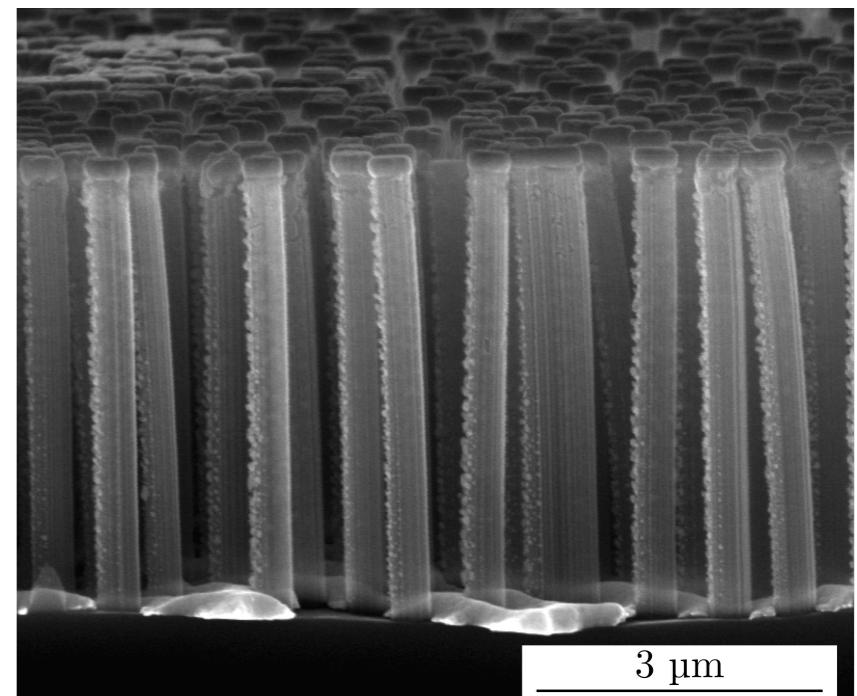
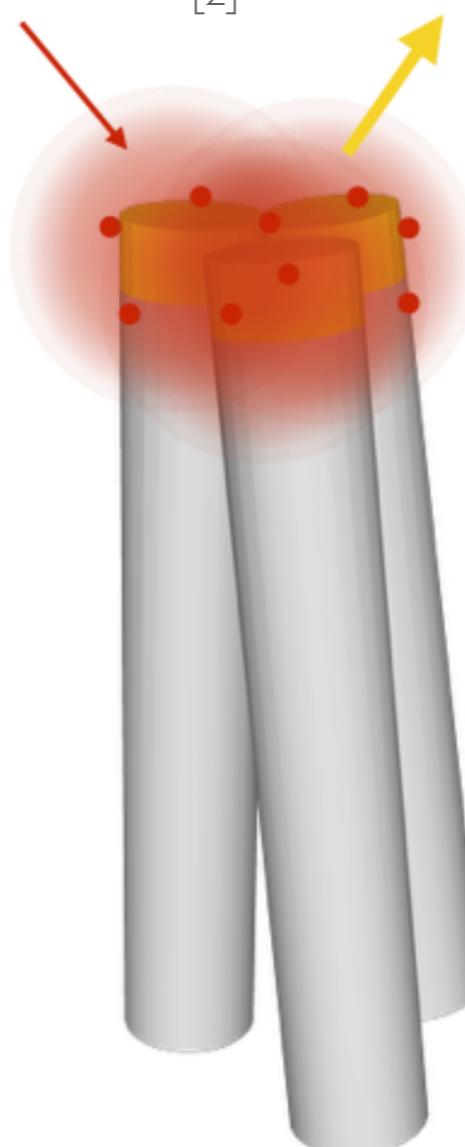


Substrate requirements:

- profitable enhancement
- good homogeneity
- high sensitivity

Hot spots engineering

- known location
- molecule position
- large-area distribution
- high density



- Probe molecule
- Nanostructure
- Enhanced near-field

Kara, S et al. RSC Adv., **2016**, 6, 93649

Cara, E. et al. Sci. Rep., **2018**, 8, 11305

[1] Wang, A. et al. Materials, **2015**, 8

[2] Fränzl, M. et al. J. Phys. Chem. C, **2018**, 122

[3] Hu, Y. et al. ACS Nano, **2010**, 4, 10

[4] Wells, S. et al. Chem. Commun., **2011**, 47

[5] Lee, S. et al. Chem. Mater., **2013**, 25, 12⁴

FABRICATION STRATEGY: Au-COATED SiNWs

NSL

Nanospheres lithography:

- large area

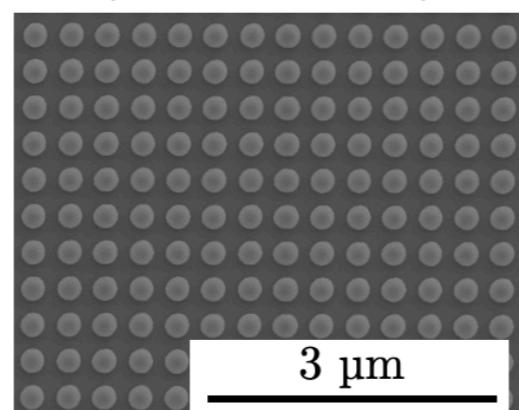
MACE

+

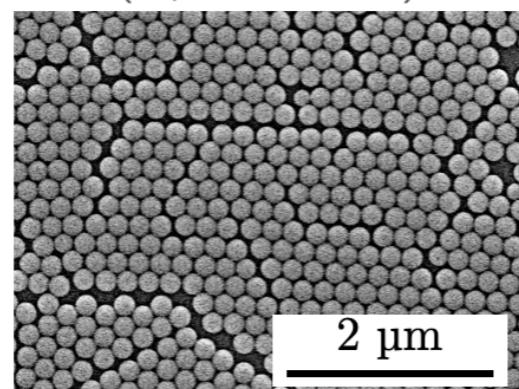
Metall-assisted chemical etching:

- high aspect ratio

Optical lithography
(5 mm – 800 nm)

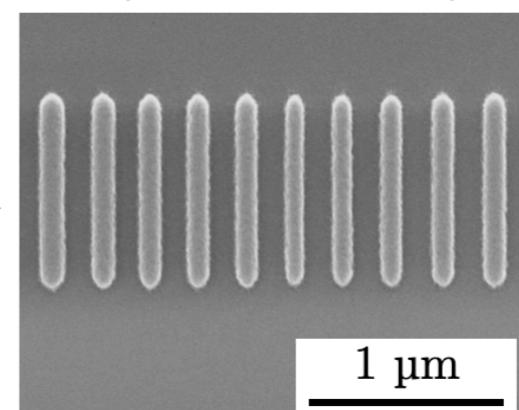


Nanospheres lithography
(2 μm – 80 nm)

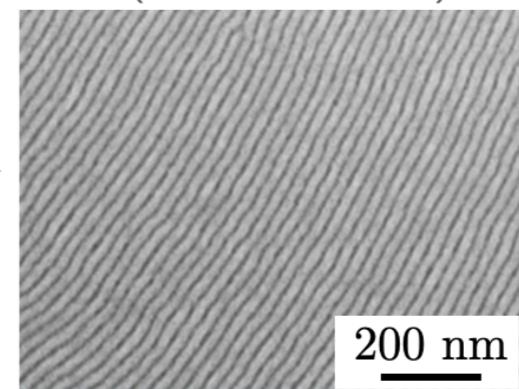


Top-down

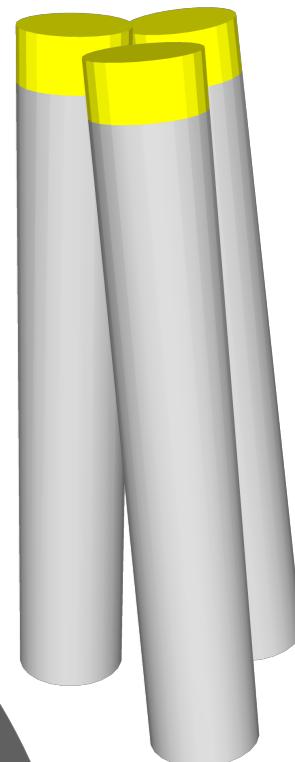
Electron beam lithography
(500 μm – 50 nm)



Block copolymers lithography
(40 nm – 10 nm)

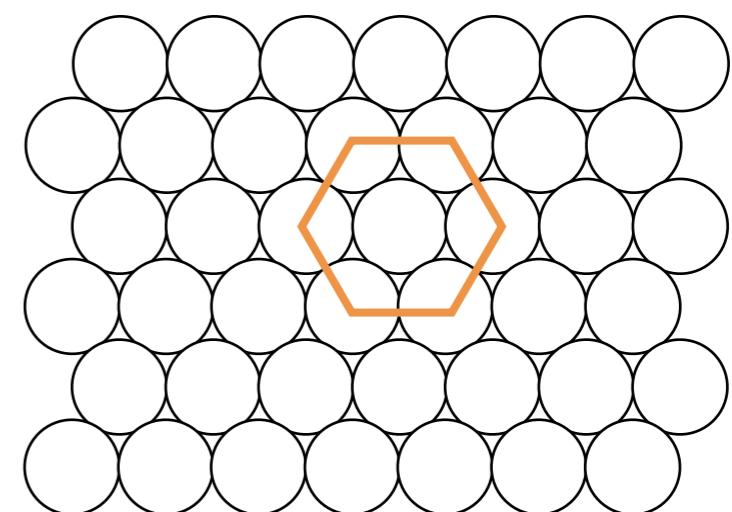
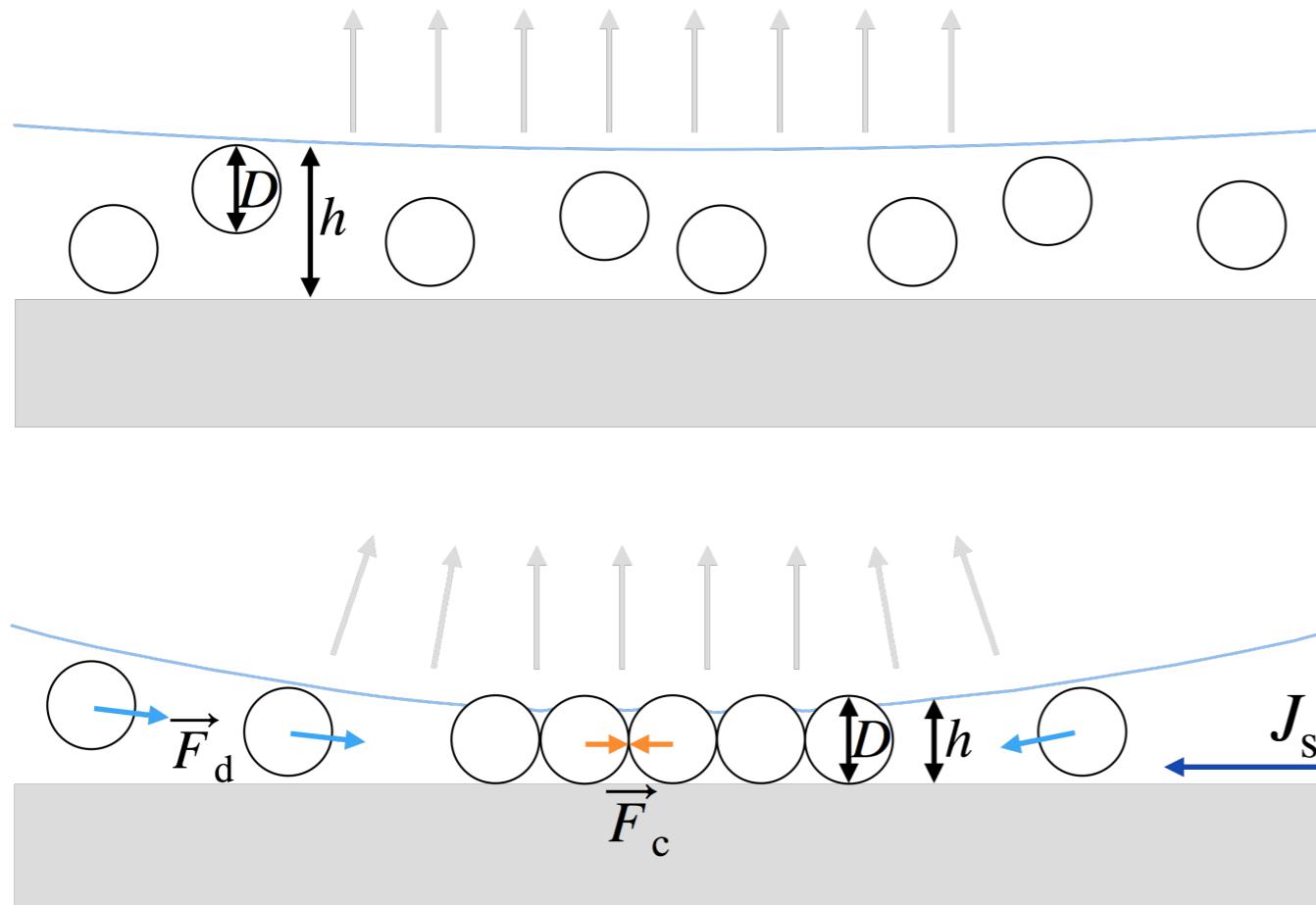


Bottom-up



NANOSPHERES LITHOGRAPHY

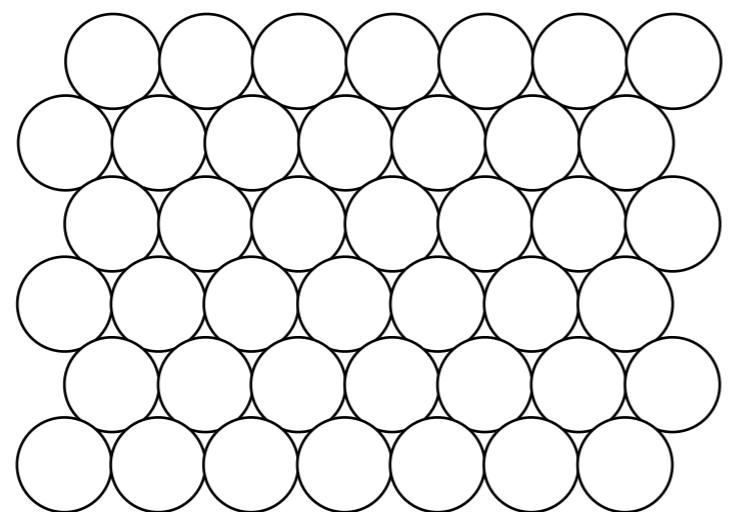
- Self-assembly driven by capillary forces in a thin wetting film on a solid substrate
- Hexagonal close-packed (**HCP**) symmetry: highest packing density



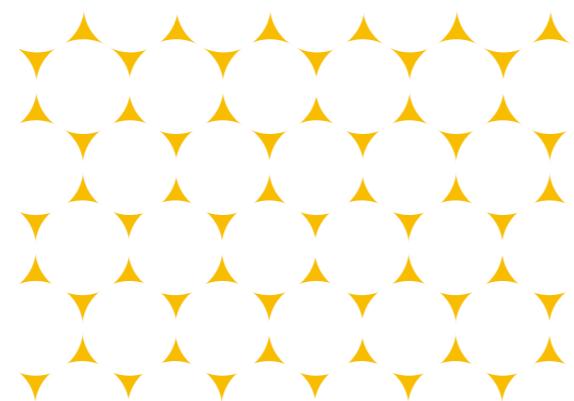
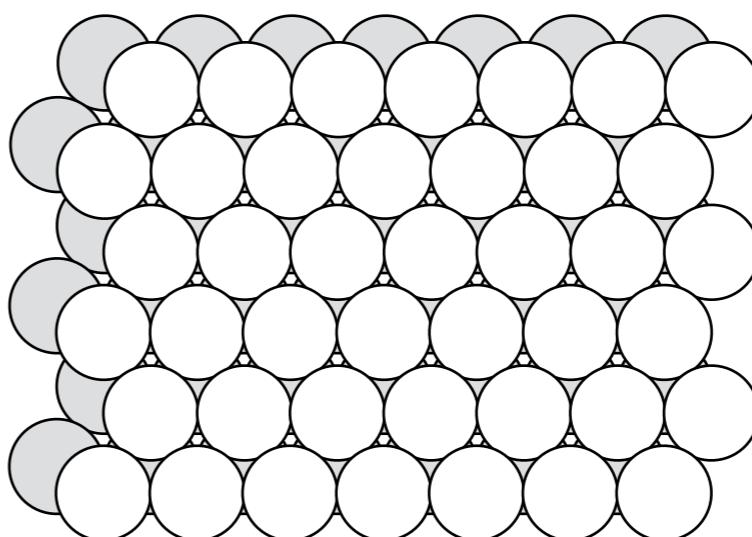
NANOSPHERES LITHOGRAPHY

- Self-assembly driven by capillary forces in a thin wetting film on a solid substrate
- Hexagonal close-packed (**HCP**) symmetry: highest packing density

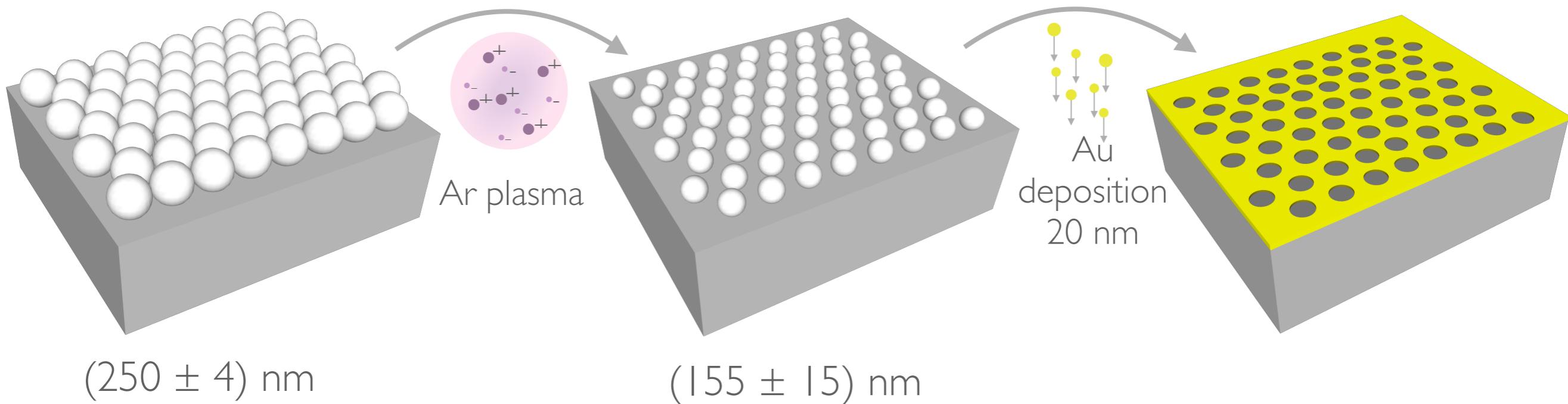
Monolayer



Bilayer



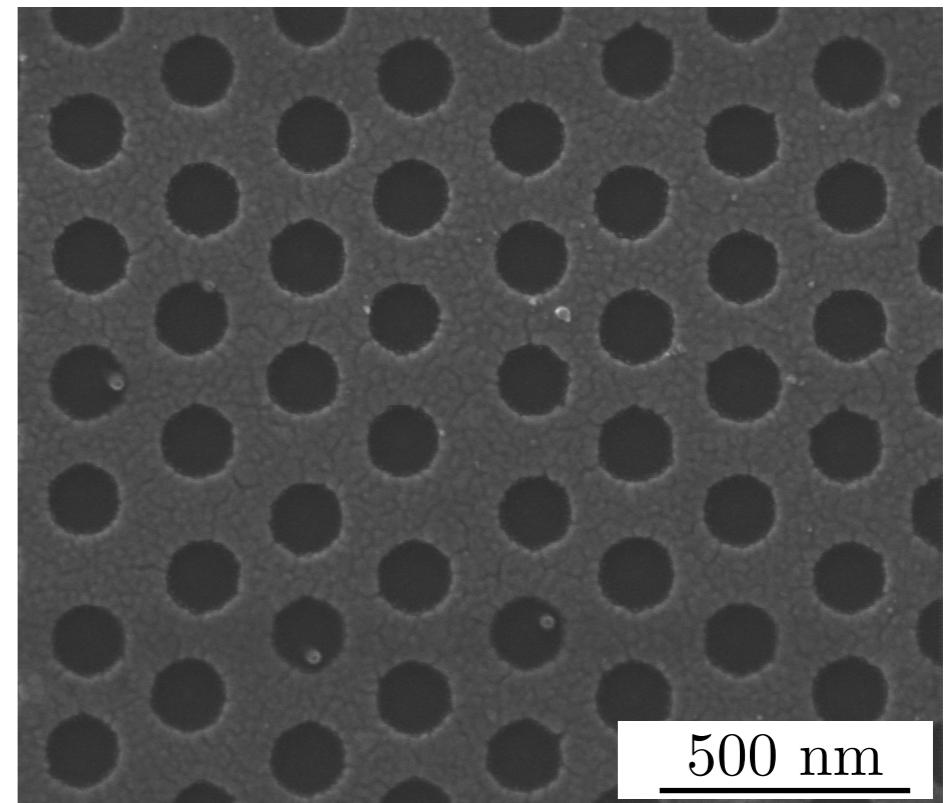
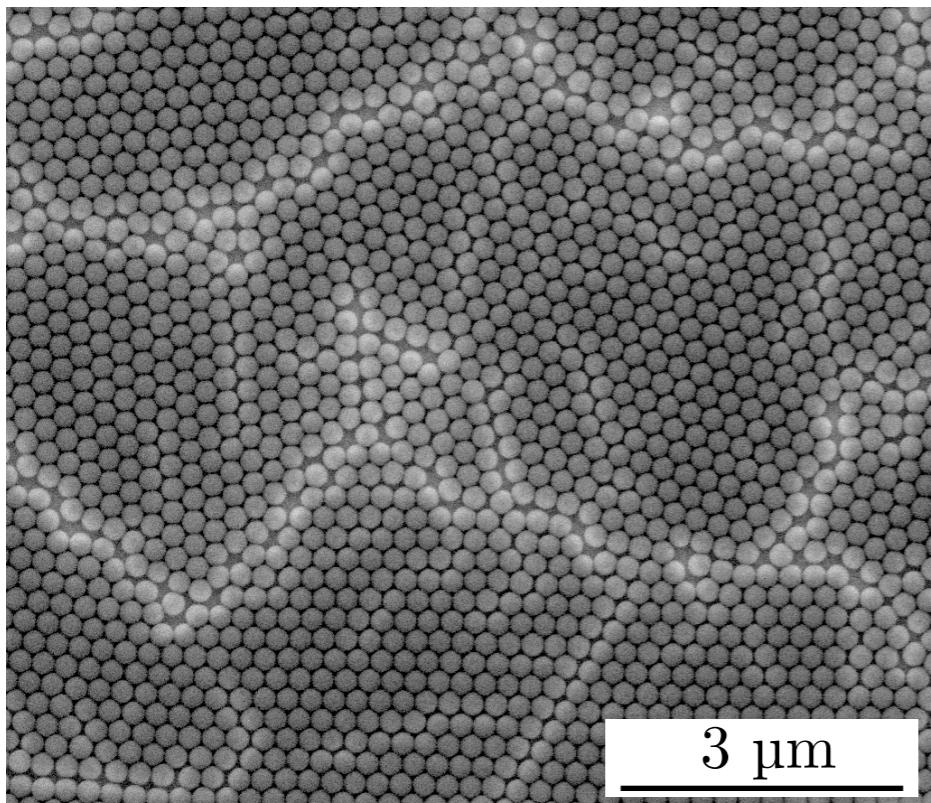
FABRICATION STRATEGY: NSL



(250 ± 4) nm

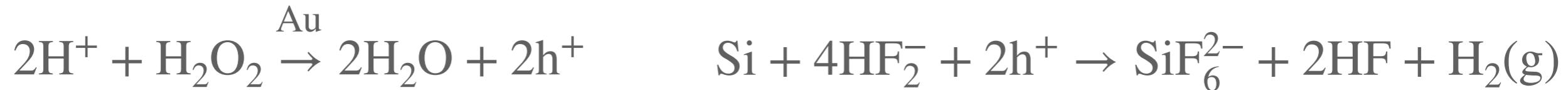
(155 ± 15) nm

Au
deposition
20 nm

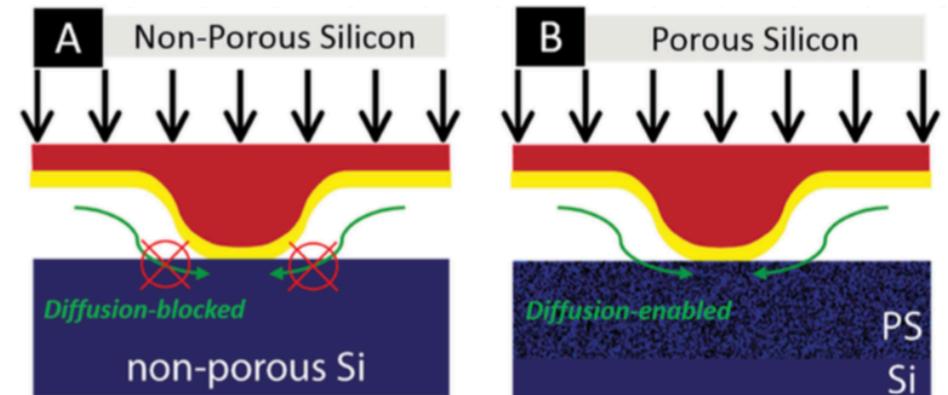


METAL-ASSISTED CHEMICAL ETCHING

- Anisotropic wet etching of semiconductors
- Oxidising agent + catalytic metal + etching reactant



Azeredo, B. et al., Adv. Funct. Mater., **2016**, 26

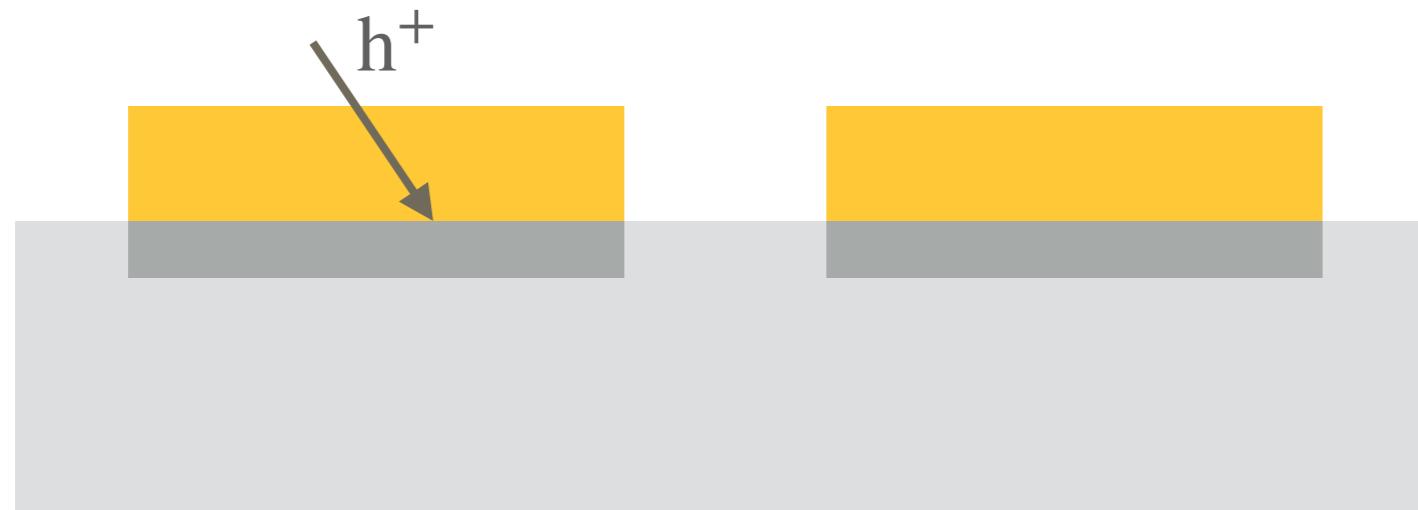
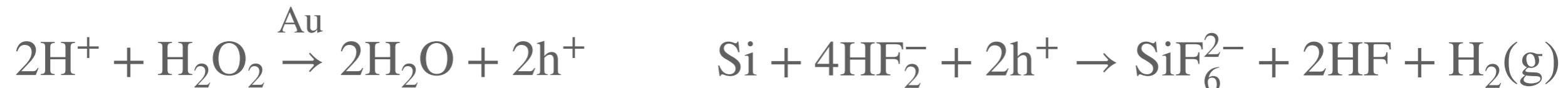


* model demonstrate in Geyer, N. et al., J. Phys. Chem. C, **2012**, 116

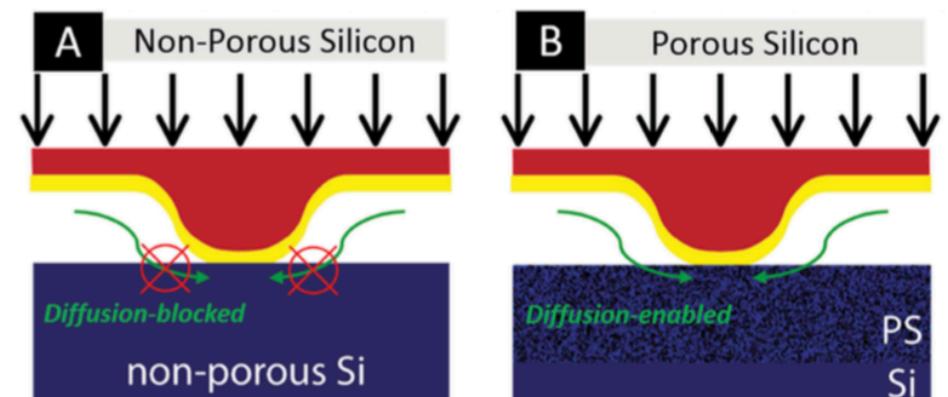
- **High** and tunable **etch rate**: μm -long structures in few minutes
- 10 nm/h in off-metal areas

METAL-ASSISTED CHEMICAL ETCHING

- Anisotropic wet etching of semiconductors
- Oxidising agent + catalytic metal + etching reactant



Azeredo, B. et al., Adv. Funct. Mater., **2016**, 26

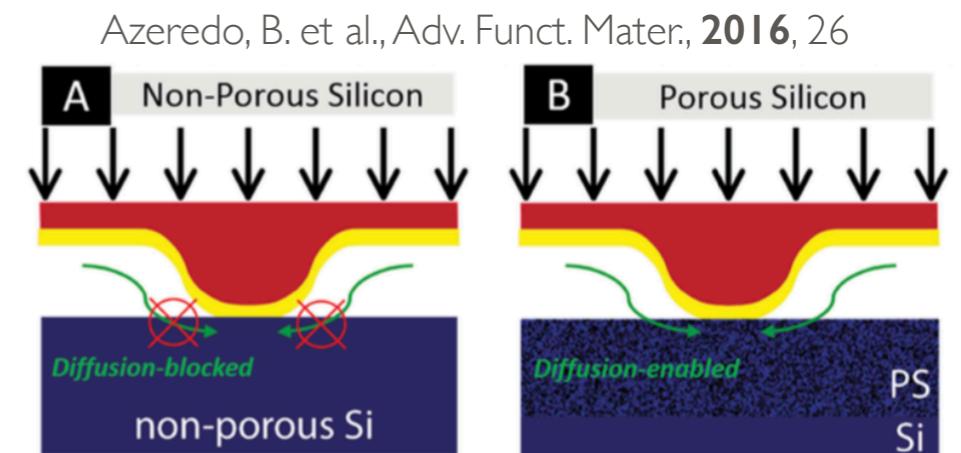
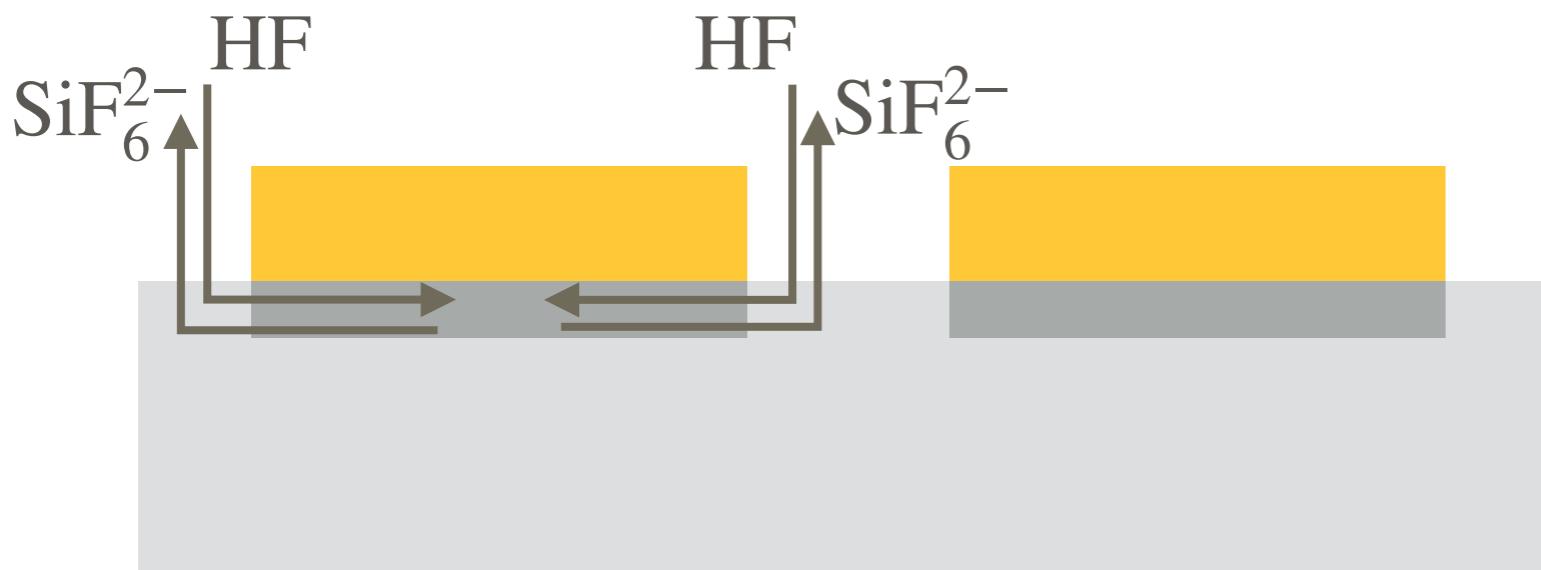
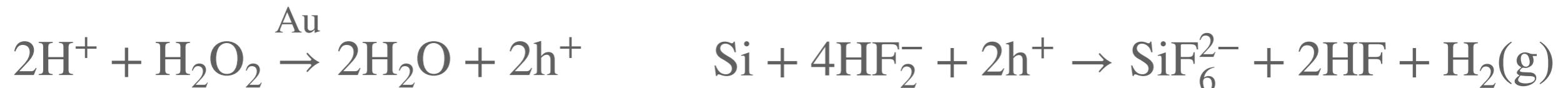


* model demonstrate in Geyer, N. et al., J. Phys. Chem. C, **2012**, 116

- **High** and tunable **etch rate**: μm -long structures in few minutes
- 10 nm/h in off-metal areas

METAL-ASSISTED CHEMICAL ETCHING

- Anisotropic wet etching of semiconductors
- Oxidising agent + catalytic metal + etching reactant

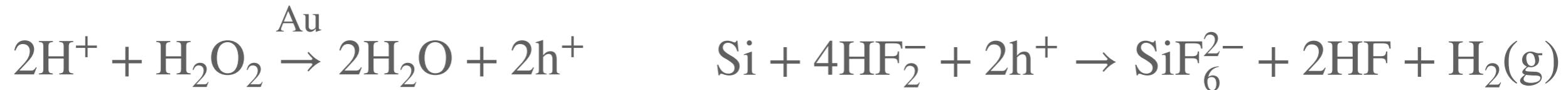


* model demonstrate in Geyer, N. et al., J. Phys. Chem. C, **2012**, 116

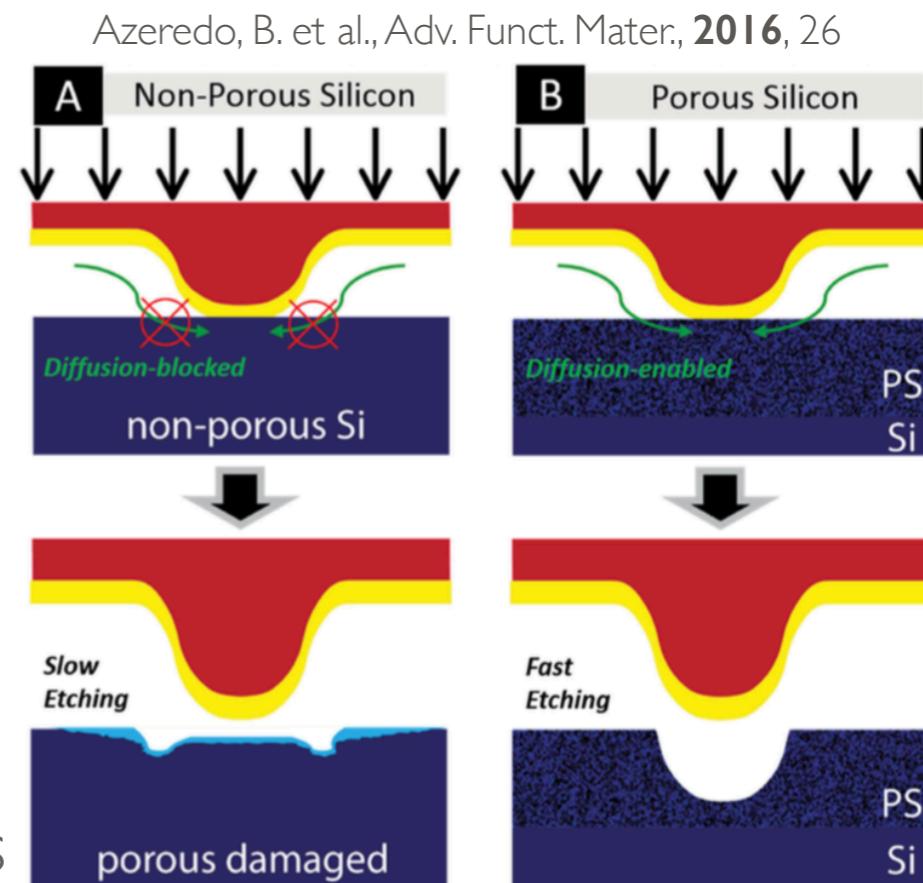
- **High** and tunable **etch rate**: μm-long structures in few minutes
- 10 nm/h in off-metal areas

METAL-ASSISTED CHEMICAL ETCHING

- Anisotropic wet etching of semiconductors
- Oxidising agent + catalytic metal + etching reactant

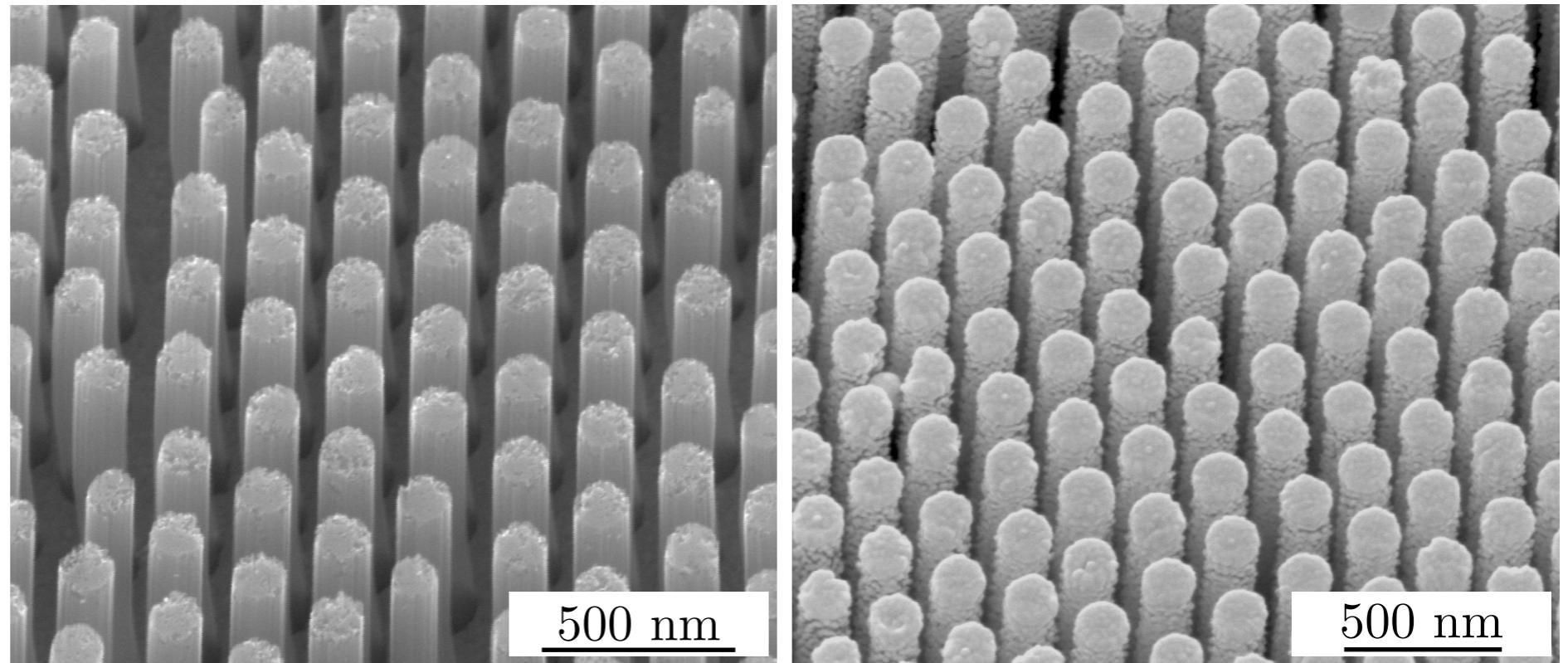
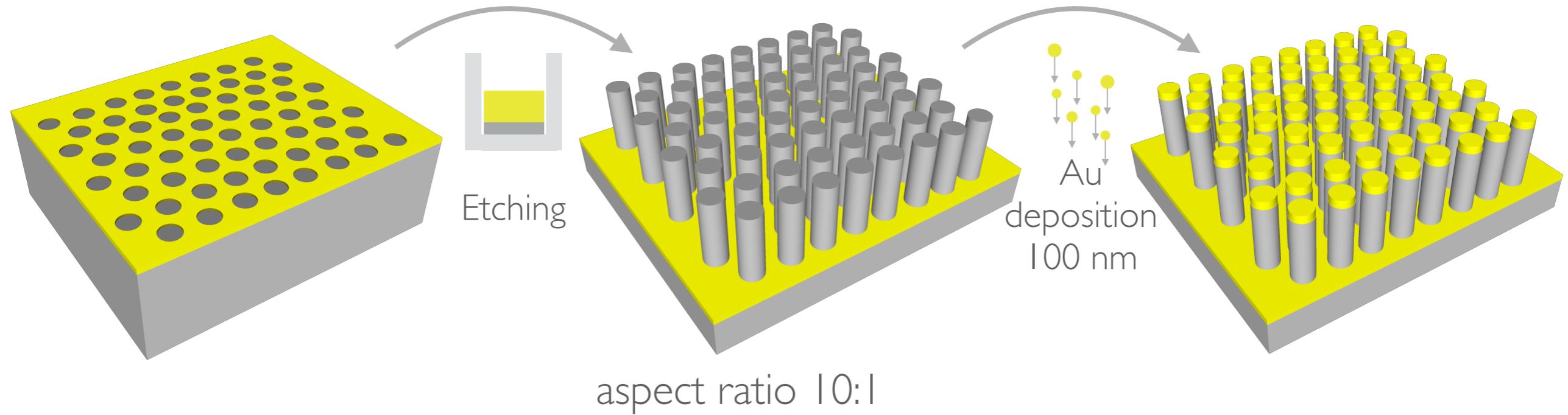


* model demonstrate in Geyer, N. et al., J. Phys. Chem. C, 2012, 116

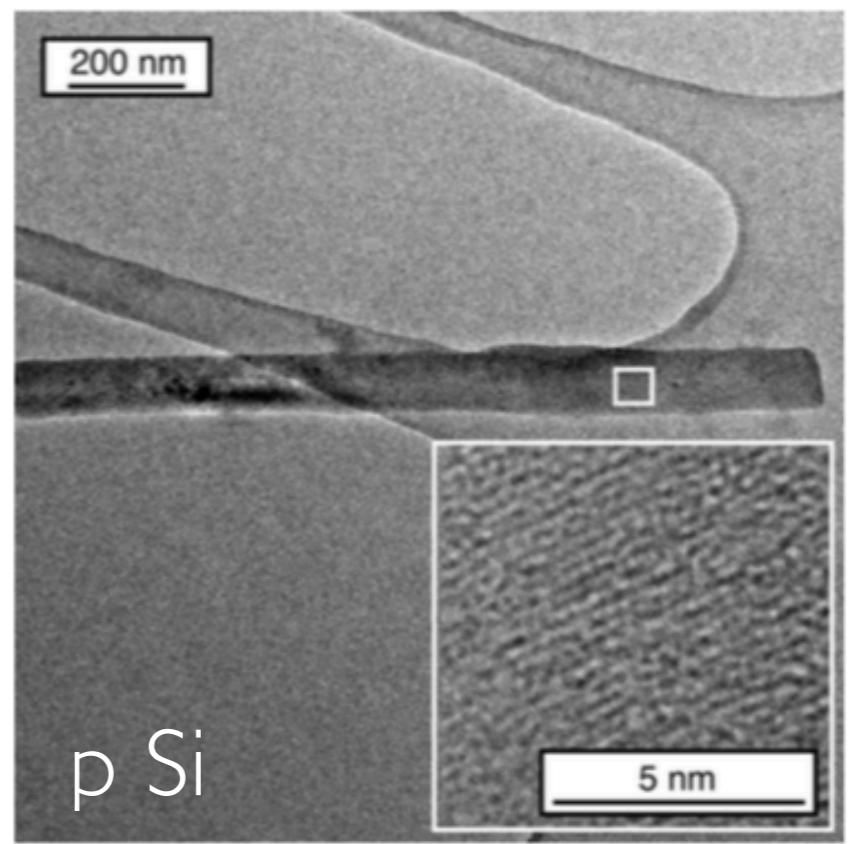
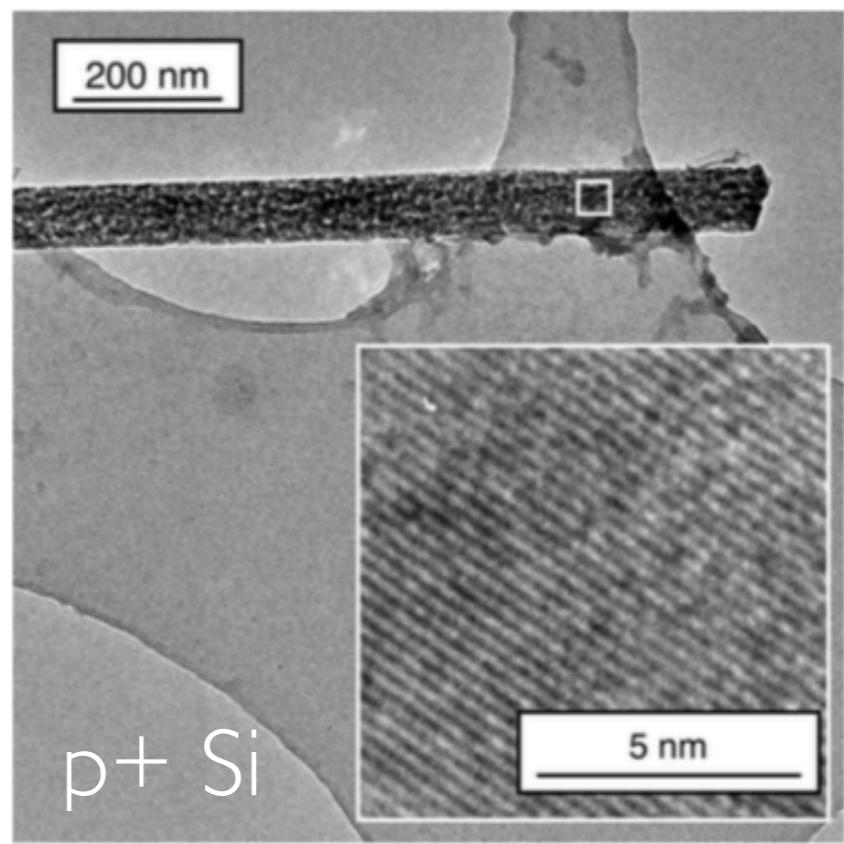
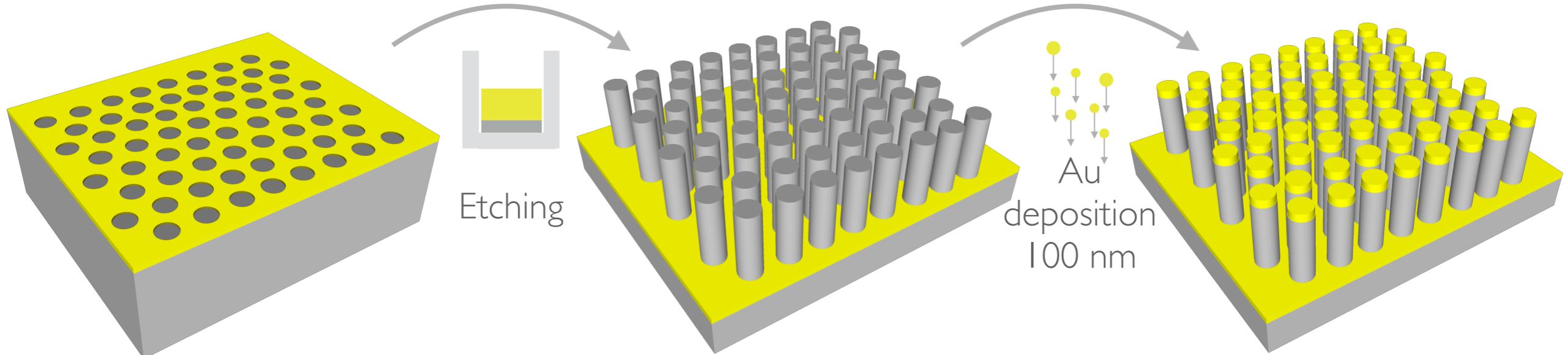


- **High** and tunable **etch rate**: μm -long structures in few minutes
- 10 nm/h in off-metal areas

FABRICATION STRATEGY: MACE



FABRICATION STRATEGY: MACE



D'Ortenzi, L et al. Nanoscale Res. Lett., **2016**, 11, 468

FABRICATION STRATEGY: Au-COATED SiNWs

NSL

Nanospheres lithography:

- large area

+

MACE

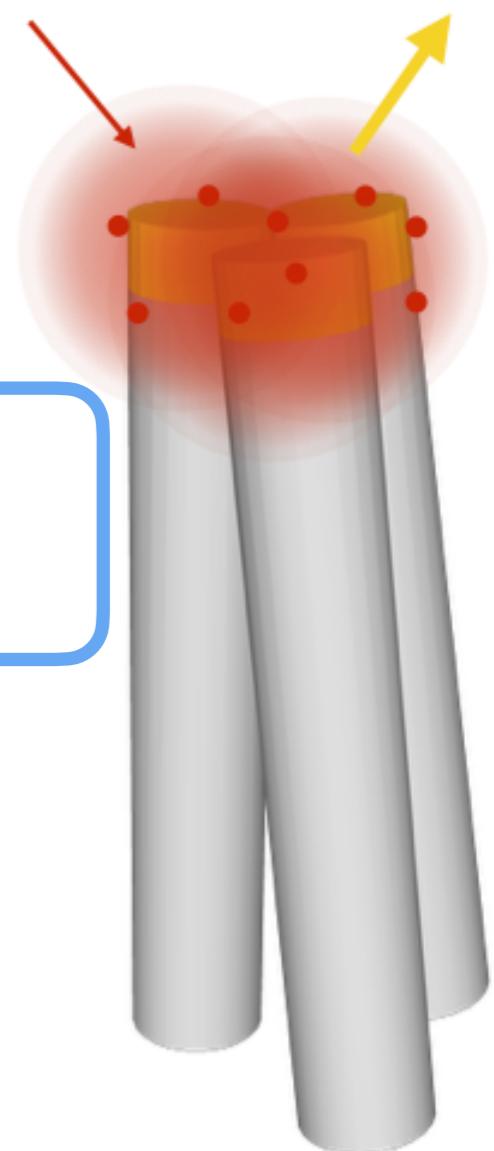
Metal-assisted chemical etching:

- high aspect ratio

Objectives of fabrication

- maximise the order

- induce nanowires bending
- adjust molecular trapping

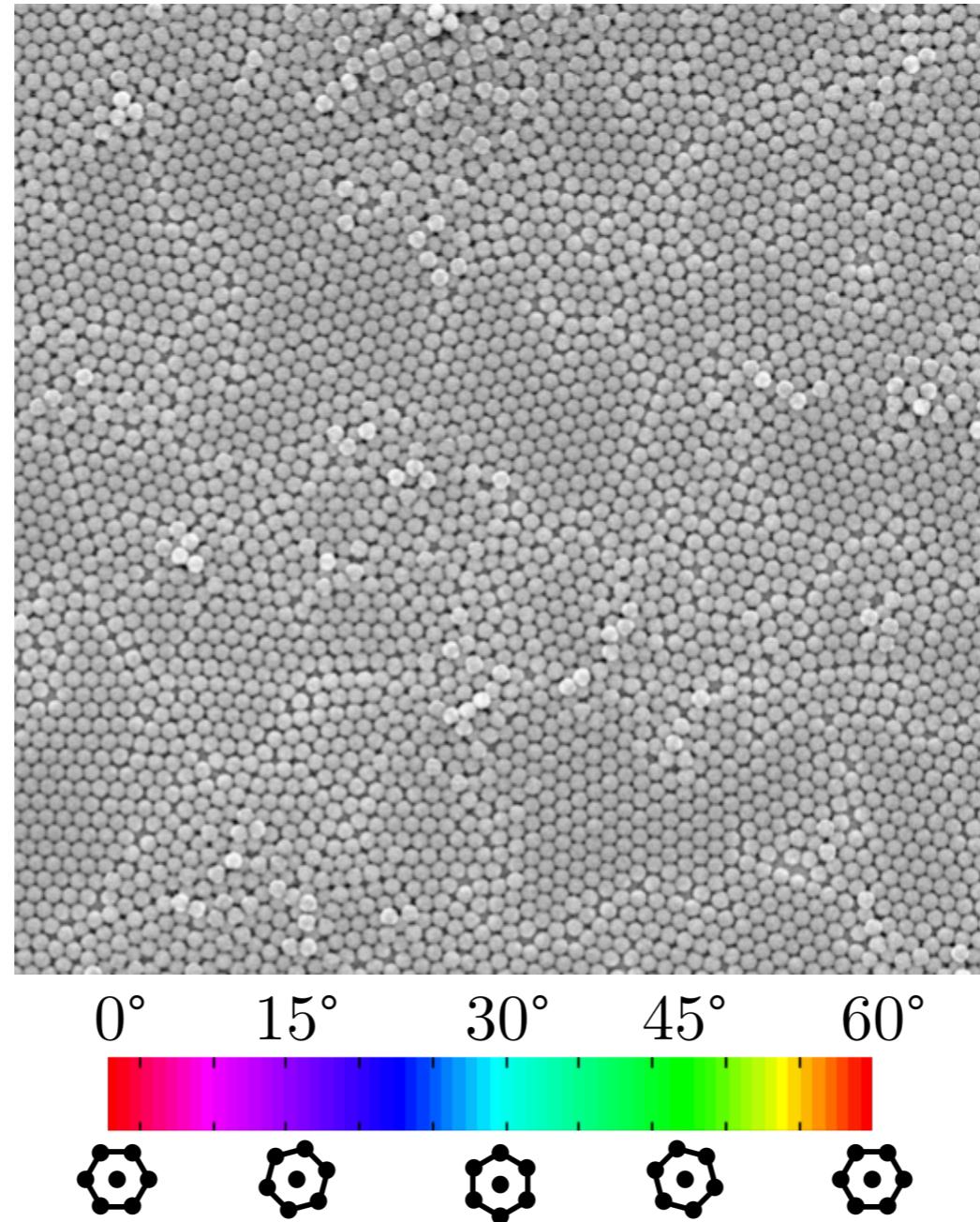


TUNING THE ORDER

- Optimisation of the HCP monolayer formation

TUNING THE ORDER

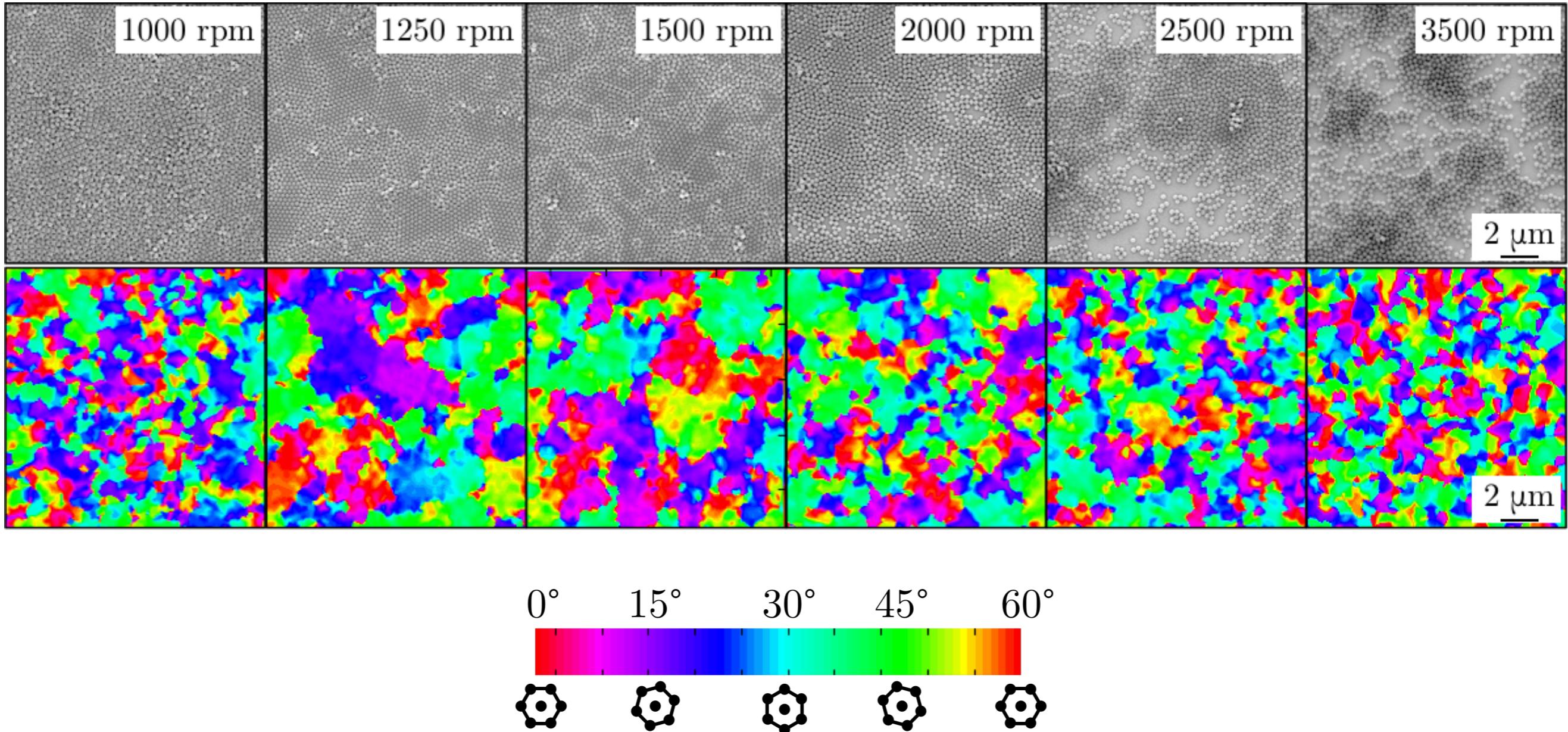
- Optimisation of the HCP monolayer formation



Cara, E. et al. Sci. Rep., 2018, 8, 11305

TUNING THE ORDER

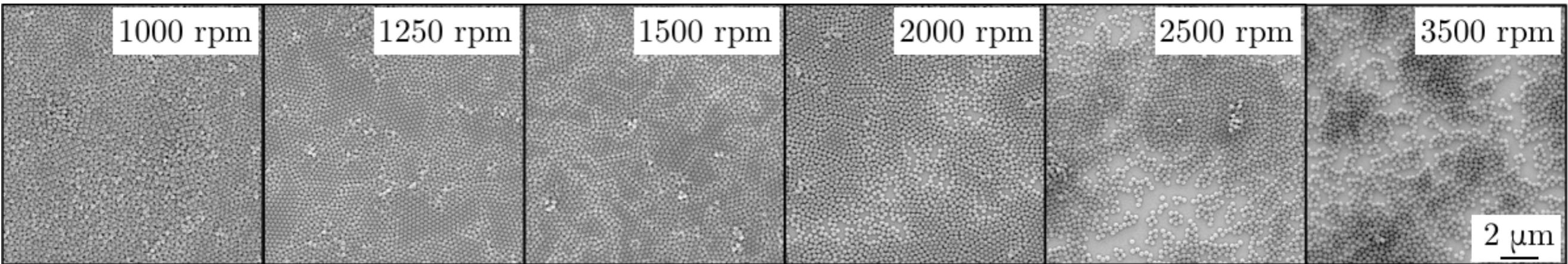
- Optimisation of the HCP monolayer formation



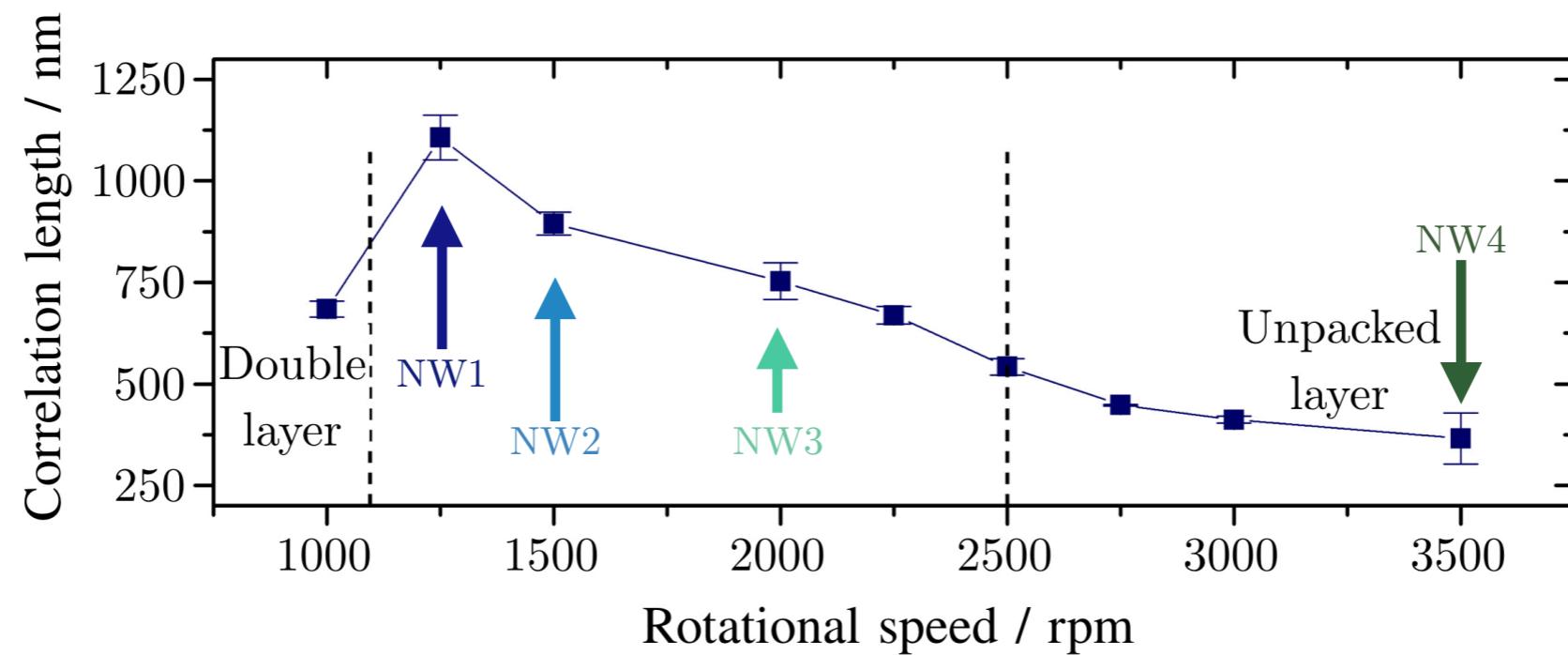
Cara, E. et al. Sci. Rep., 2018, 8, 11305

TUNING THE ORDER

- Optimisation of the HCP monolayer formation



Lowest defectivity

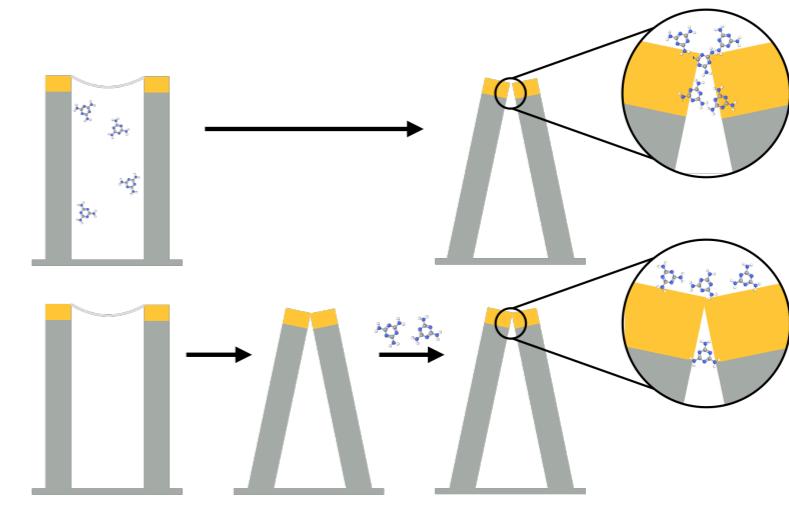
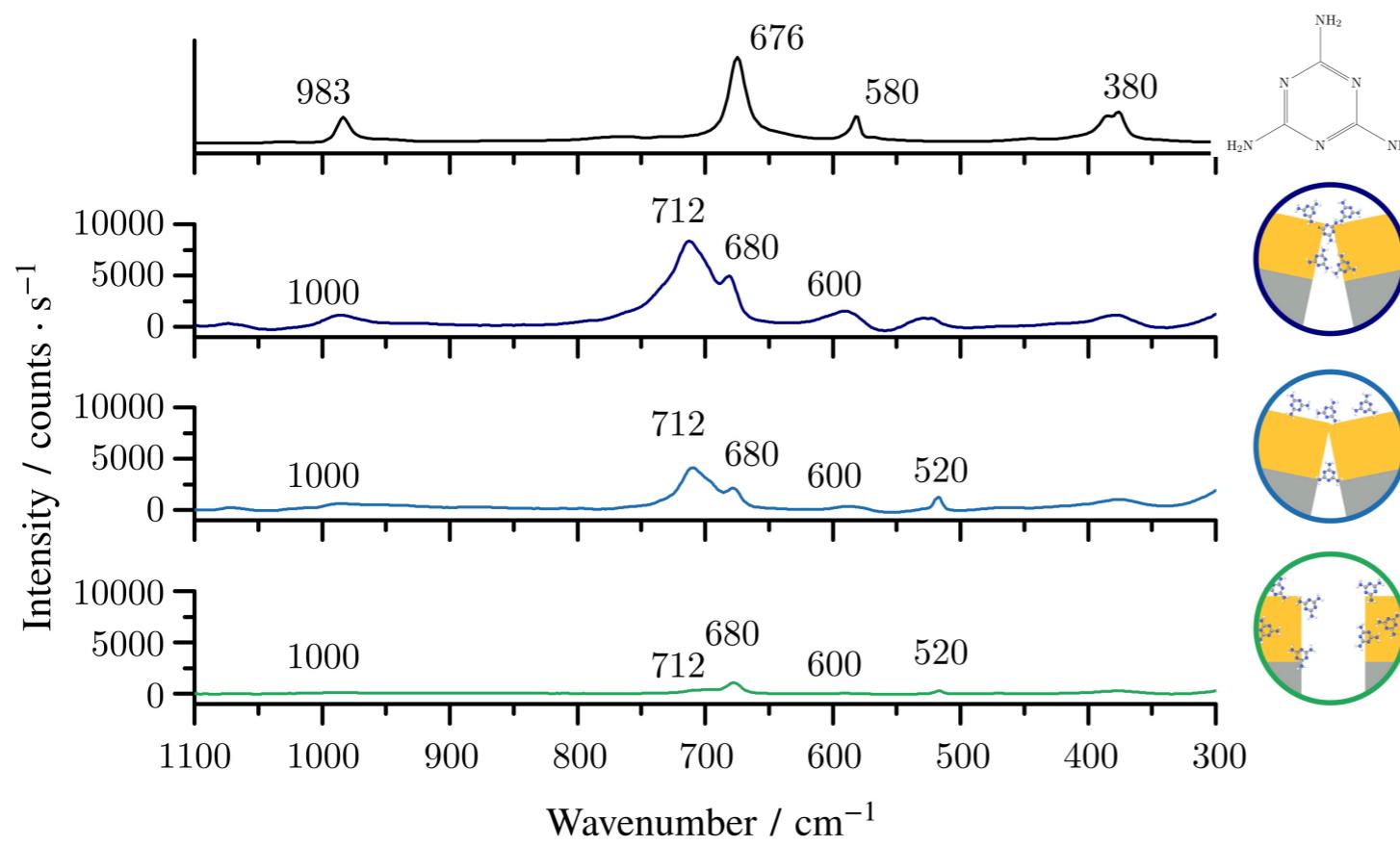
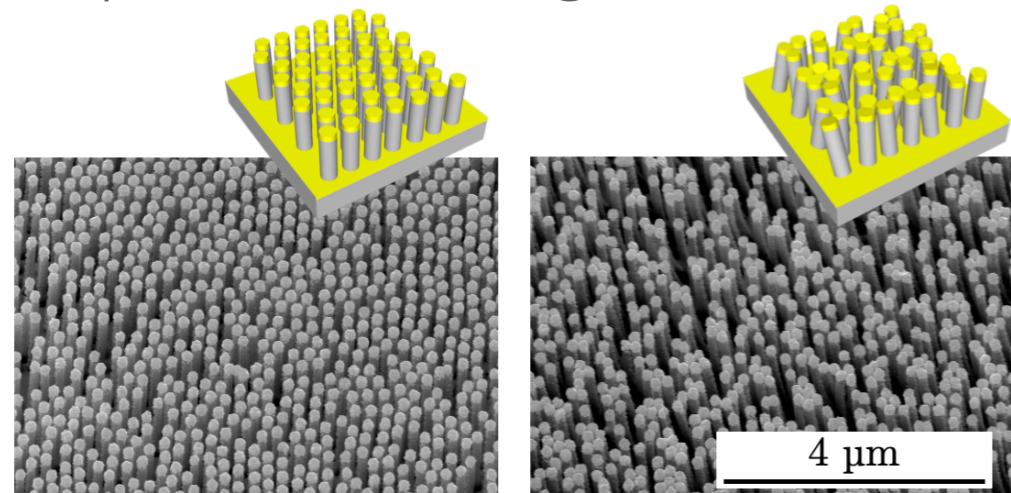


- Correlation length: quantification of the degree of order

Cara, E. et al. Sci. Rep., 2018, 8, 11305

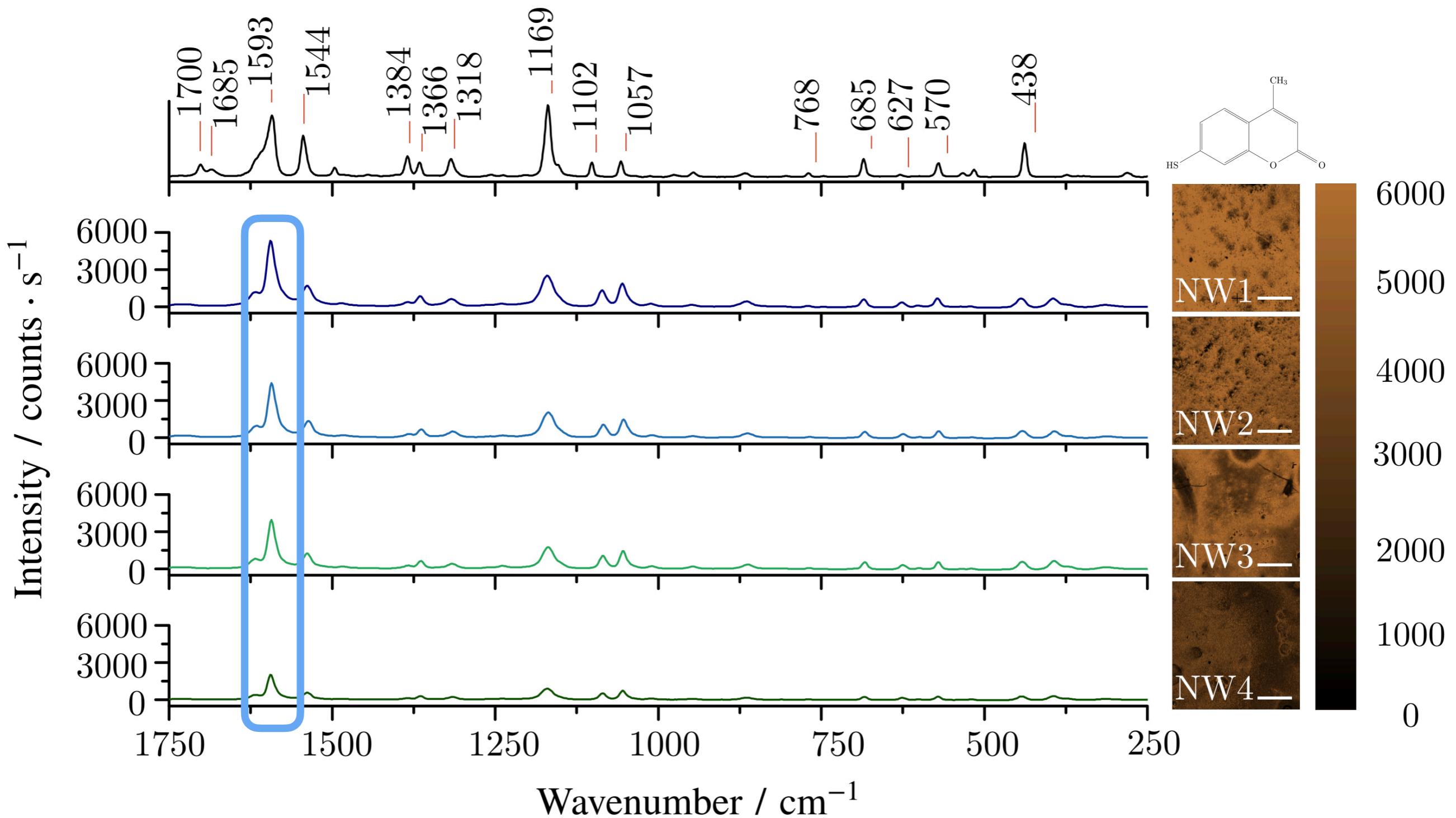
HOT SPOTS AND MOLECULES LOCATION

- Test on **different mechanical configurations**: post-deposition leaning or pre-deposition leaning



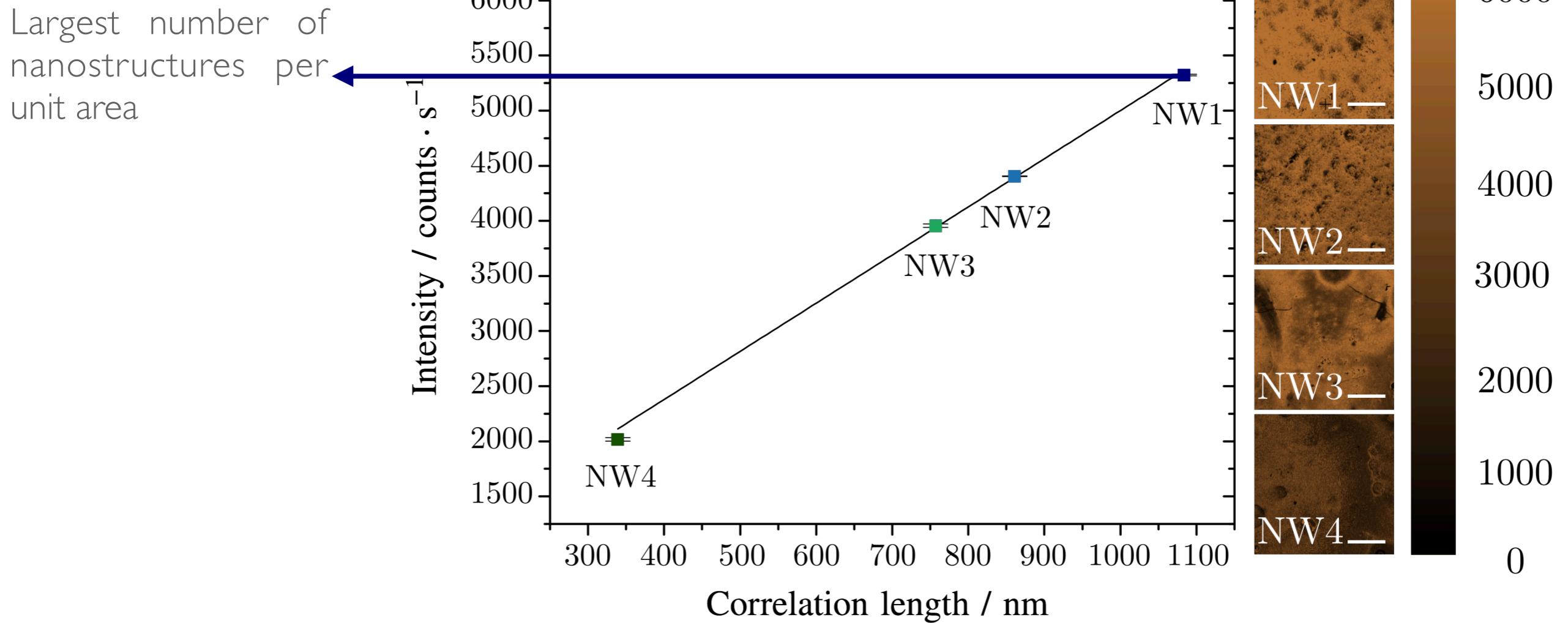
Kara, S et al. RSC Adv., 2016, 6, 93649

ORDER-DEPENDENT INTENSITY



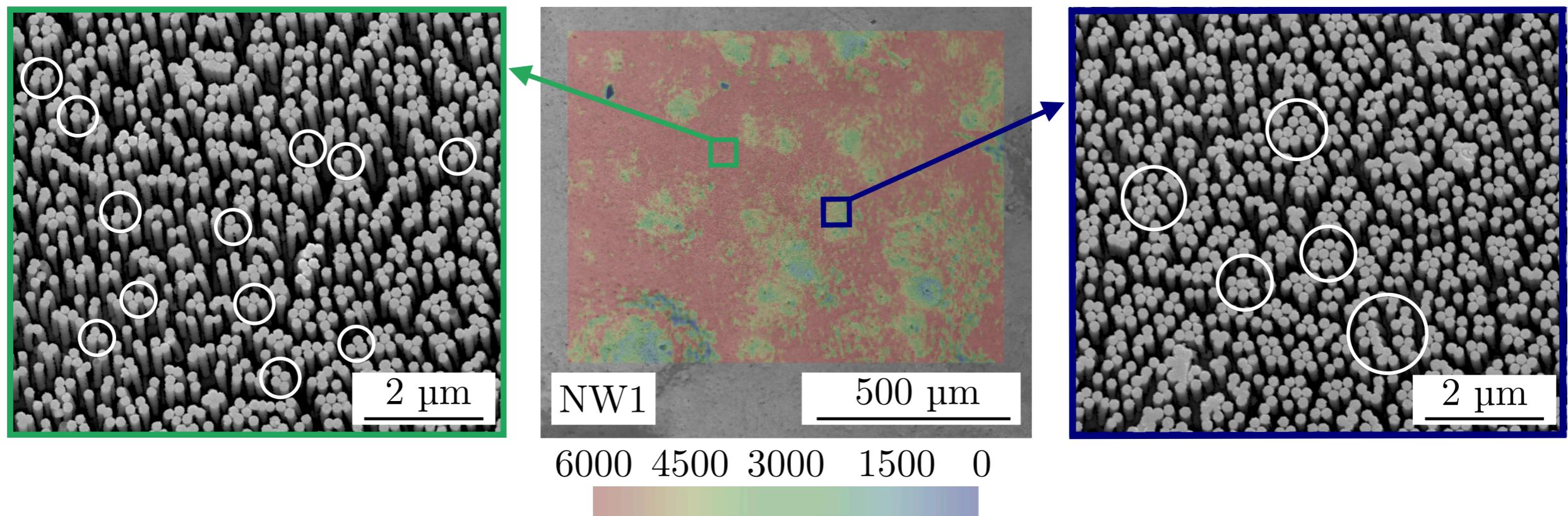
Cara, E. et al. Sci. Rep., 2018, 8, 11305

ORDER-DEPENDENT INTENSITY



HOT SPOTS MORPHOLOGY

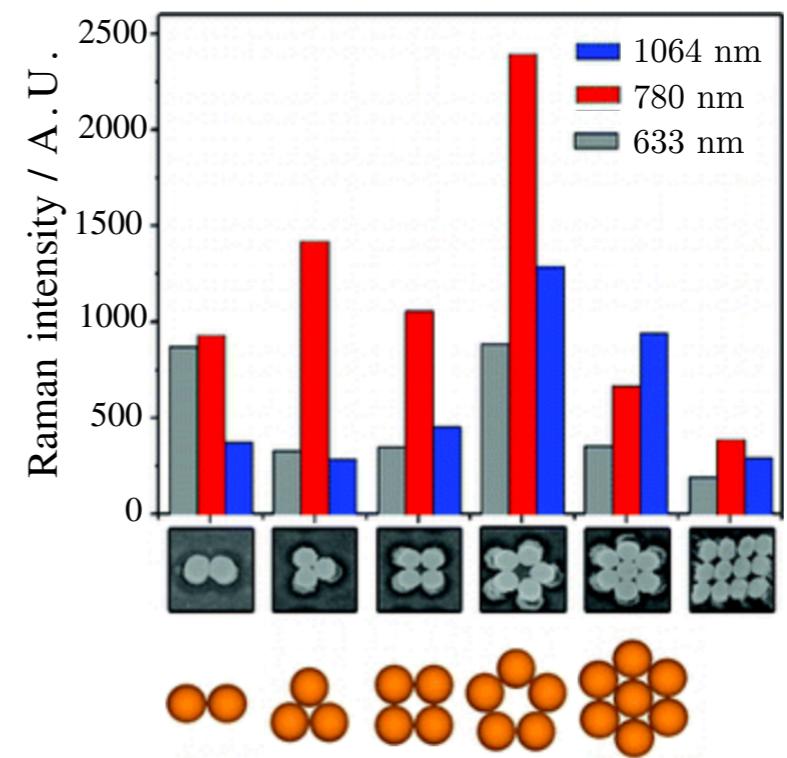
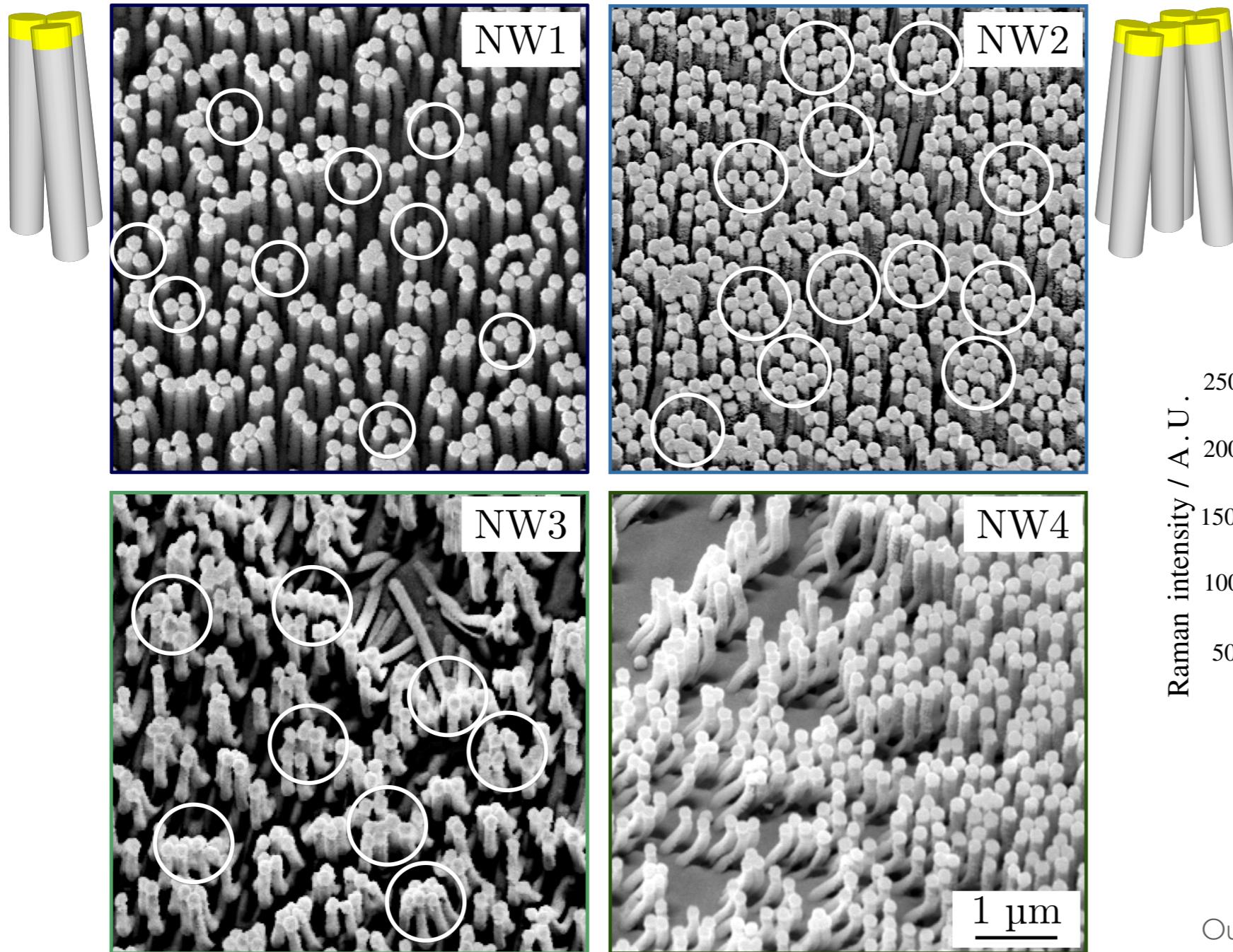
- Correlative microscopy: Raman mapping + SEM



Cara, E. et al. Sci. Rep., 2018, 8, 11305

HOT SPOTS MORPHOLOGY

- Correlative microscopy: Raman mapping + SEM



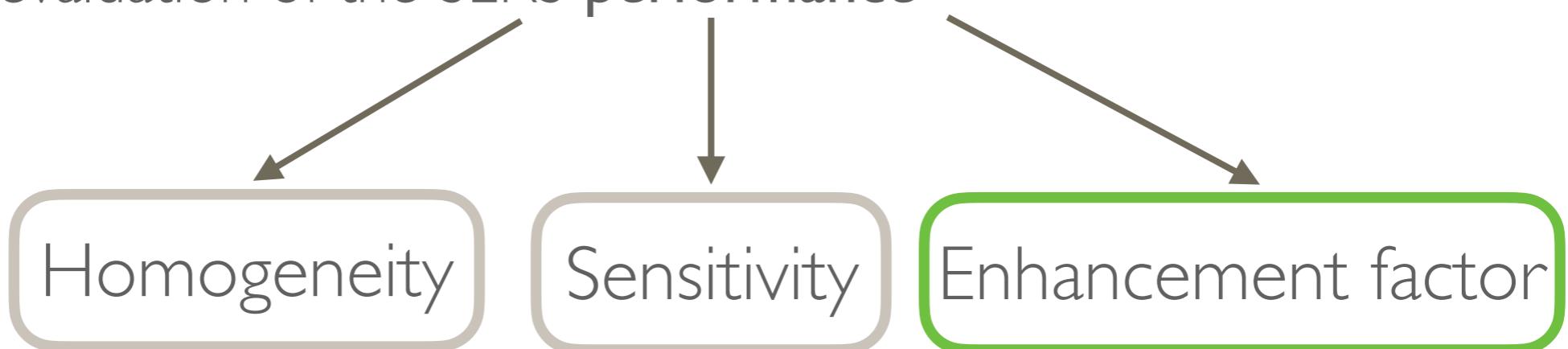
Ou, F. S. et al. Nano Lett., 2011, 11, 2538

Cara, E. et al. Sci. Rep., 2018, 8, 11305

METROLOGY FOR SERS

Surface-enhancement Raman spectroscopy (SERS)

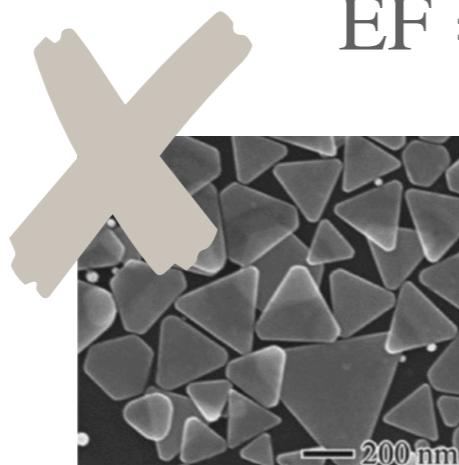
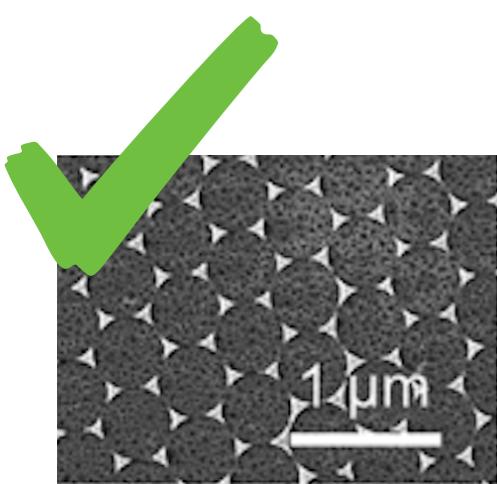
1. Efficient **fabrication** for active substrates
2. Accurate evaluation of the SERS **performance**



Essential parameter for the evaluation of SERS substrates

$$EF = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{NR}}/N_{\text{NR}}}$$

$10^3 - 10^{10}$

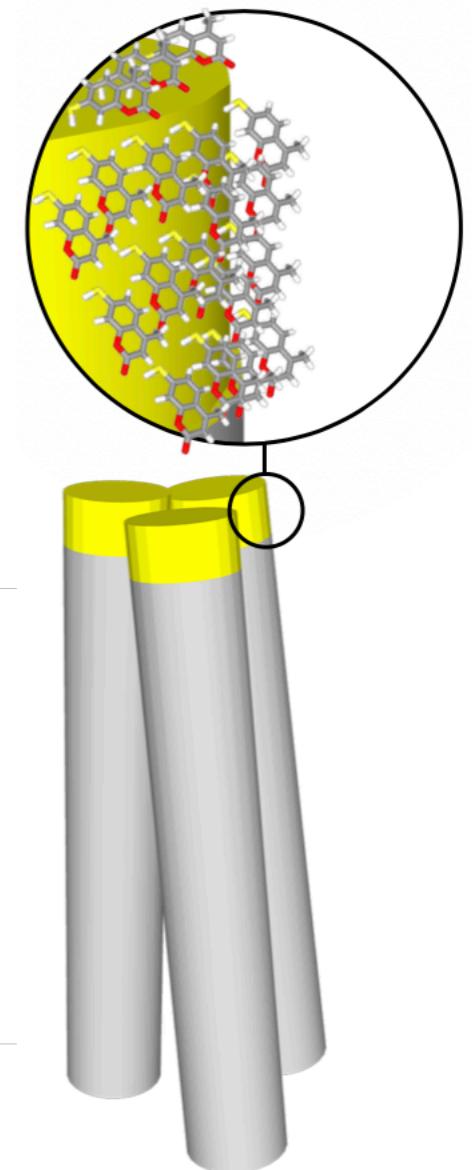
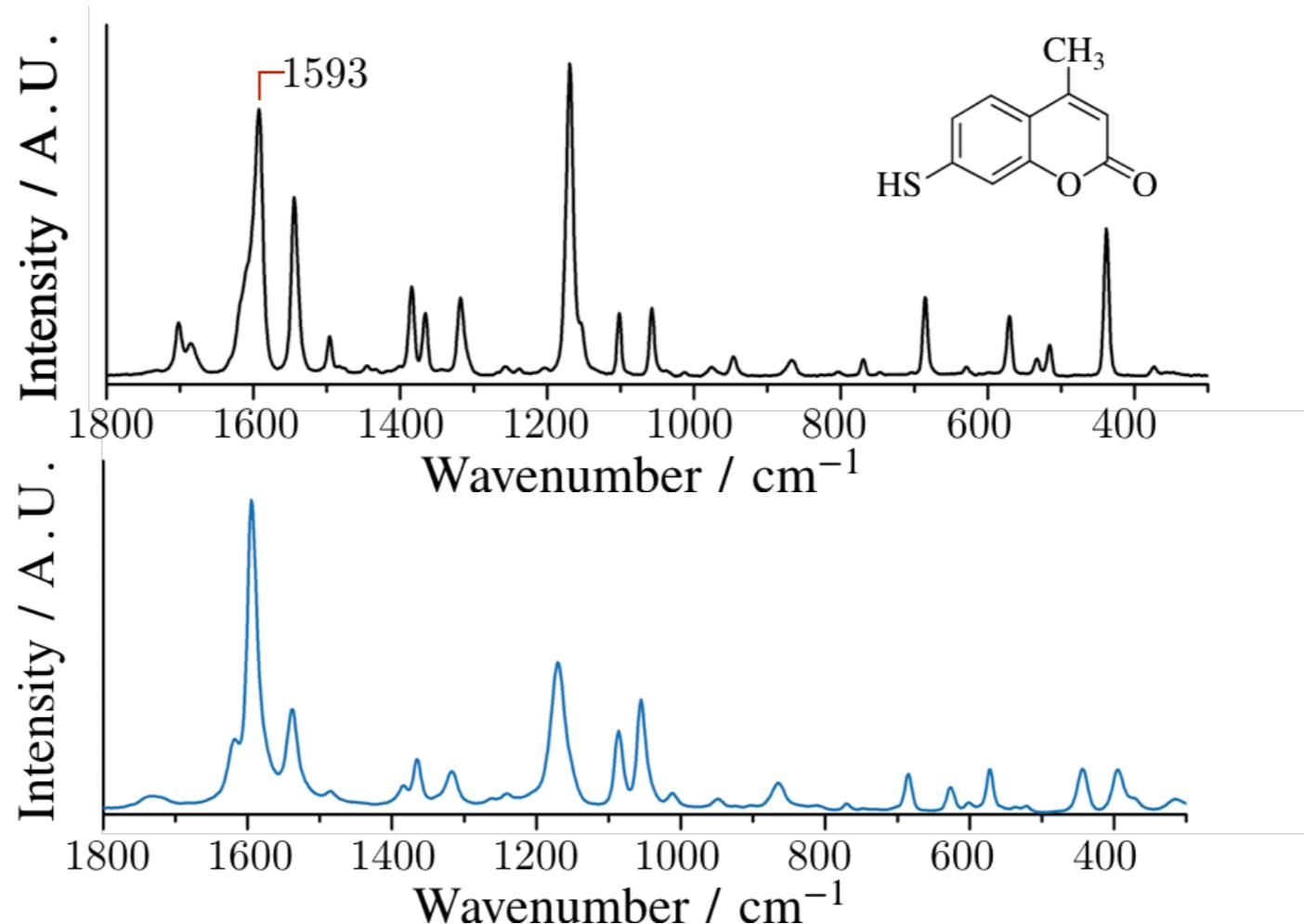


ENHANCEMENT FACTOR

$$EF = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{NR}}/N_{\text{NR}}}$$

Normal Raman (NR) conditions: in liquid measurements

- number of molecules in the probe volume $N_{\text{NR}} = c_{\text{NR}} \cdot V$
- intensity



SERS conditions:

- intensity

- number of probed molecules $N_{\text{SERS}} = \mu_{\text{mol}} \cdot A_M \cdot \mu_M \cdot A_{\text{eff}}$

Cara, E. et al. 2020, submitted

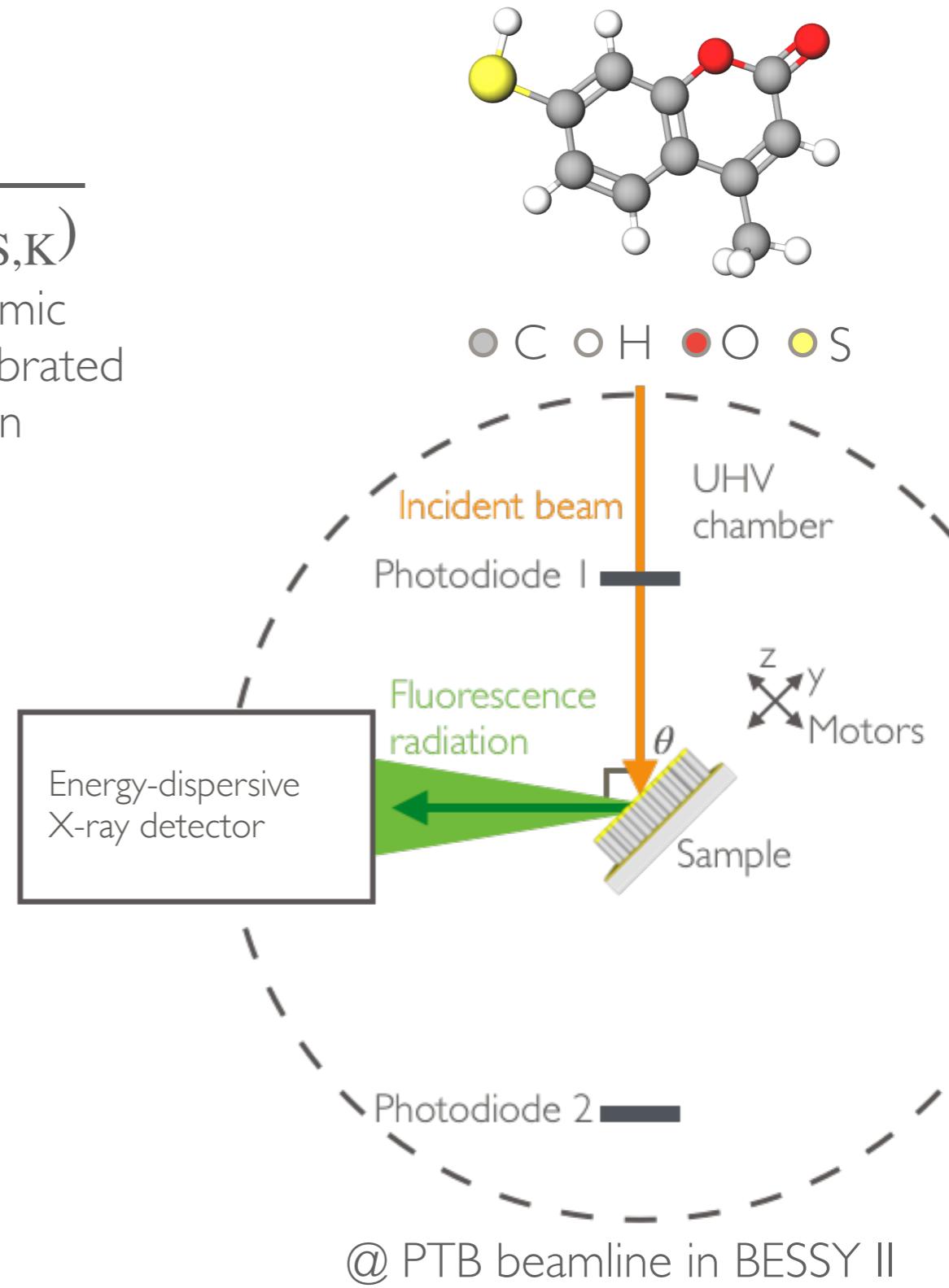
REFERENCE-FREE X-RAY FLUORESCENCE

Elemental surface density

$$\sigma_S = \frac{1}{k} \cdot N \cdot P_{S,K} \cdot \frac{1}{\tau_{S,K}(E_0) \cdot \omega_{S,K} \cdot \epsilon(E_{S,K})}$$

Photon count
for sulphur

Fundamental atomic
parameters and calibrated
instrumentation



Cara, E. et al. 2020, submitted

@ PTB beamline in BESSY II

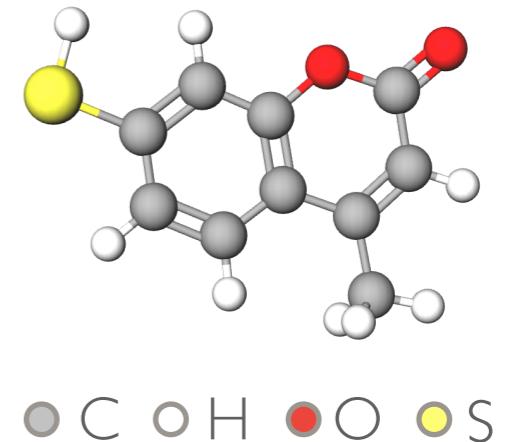
REFERENCE-FREE X-RAY FLUORESCENCE

Elemental surface density

$$\sigma_S = \frac{1}{k} \cdot N \cdot P_{S,K} \cdot \frac{1}{\tau_{S,K}(E_0) \cdot \omega_{S,K} \cdot \epsilon(E_{S,K})}$$

Photon count
for sulphur

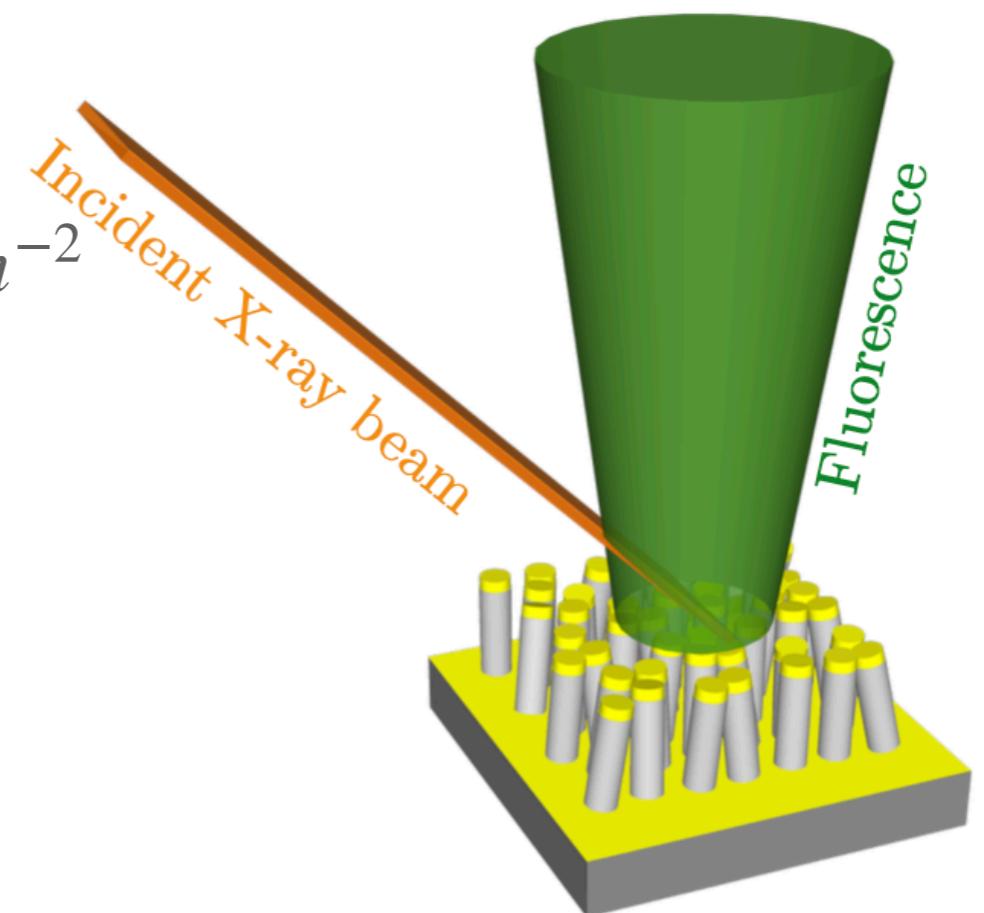
Fundamental atomic
parameters and calibrated
instrumentation



Molecular surface density

$$\mu_{\text{mol/XRF}} = \left(\sigma_S \cdot \frac{N_A}{w_S} \right) = (6.1 \pm 1.0) \cdot 10^6 \mu\text{m}^{-2}$$

$$N_{\text{SERS/XRF}} = (2.0 \pm 0.5) \cdot 10^8$$



Cara, E. et al. 2020, submitted

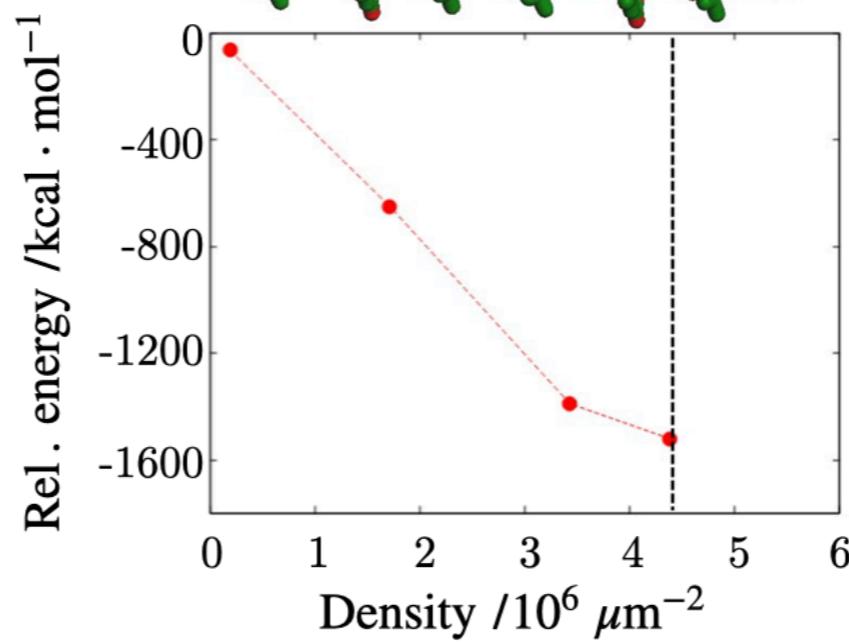
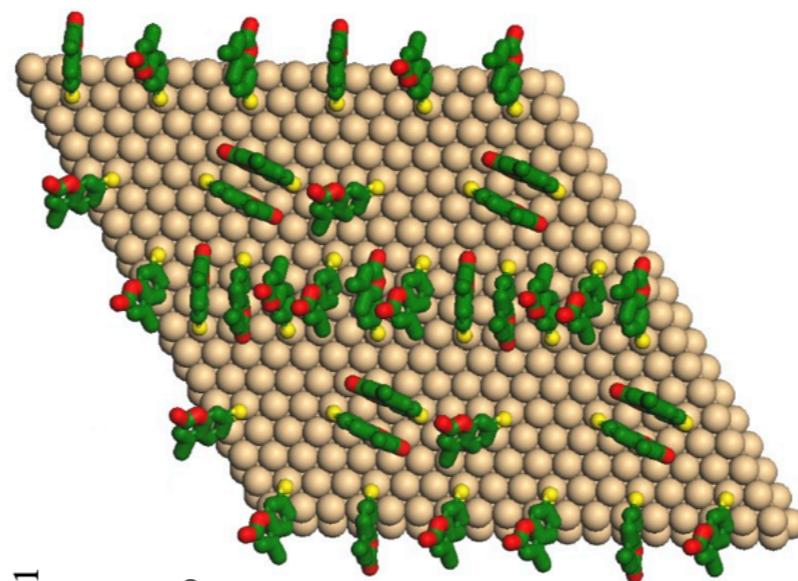
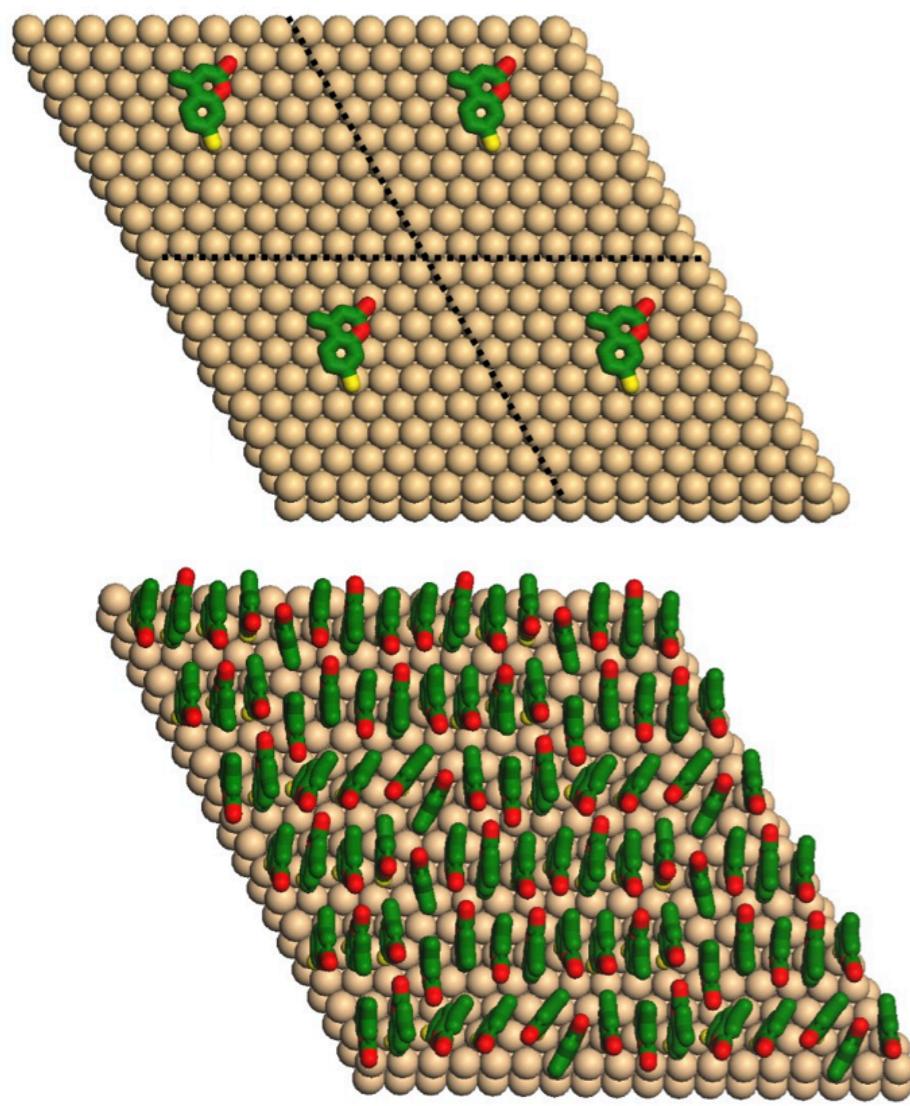
@ PTB beamline in BESSY II

THEORETICAL SIMULATIONS

- Molecular dynamics simulations: force field among the molecules

$$\mu_{\text{mol/simul}} = 4.3 \cdot 10^6 \mu\text{m}^{-2}$$

$$N_{\text{SERS/simul}} = (1.4 \pm 0.3) \cdot 10^8$$



$$EF_{\text{simul}} = (1.9 \pm 0.5) \cdot 10^5$$

$$EF_{\text{XRF}} = (1.4 \pm 0.4) \cdot 10^5$$

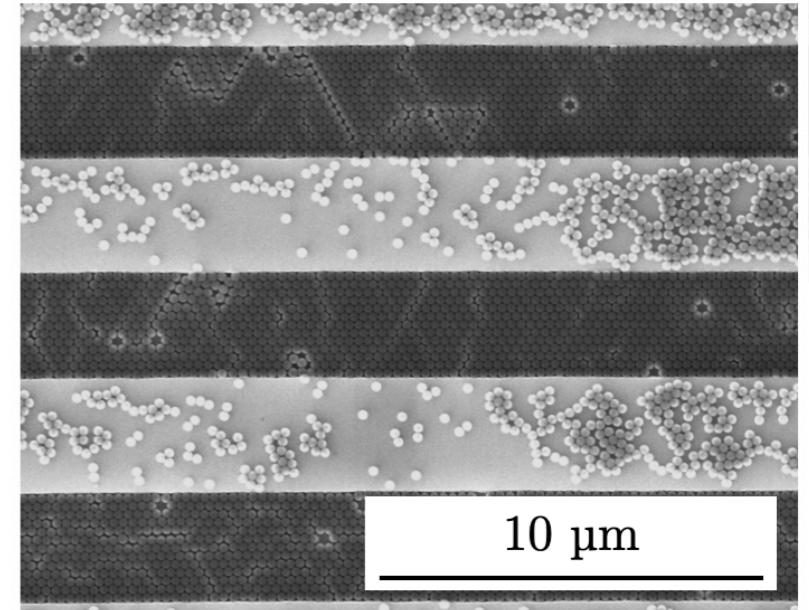
Supported by analytical method traceable to the SI, fully calibrated instrumentation

FINAL REMARKS

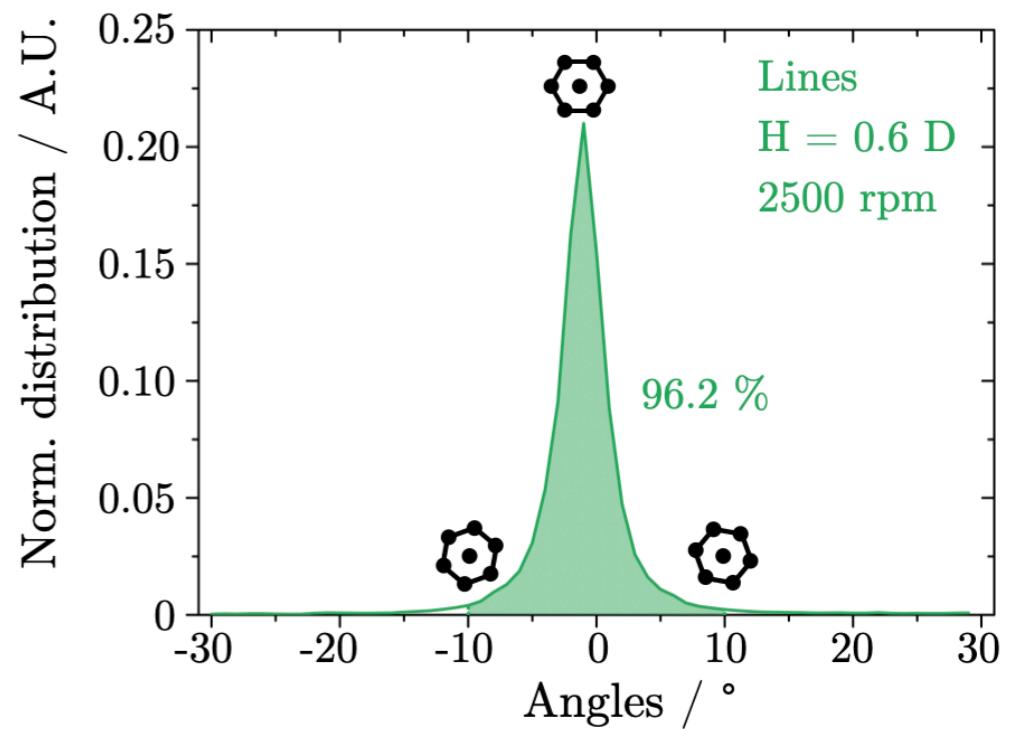
- Self-assembly-based fabrication: **long-range-ordered** and **flexible** nanostructures over **large area**
- Morphological manipulation for hot spots
- Metrological evaluation of the **substrate efficiency**
 - enhancement factor: traceable calibrated RF-XRF for **molecule quantification**

FINAL REMARKS

- Self-assembly-based fabrication: **long-range-ordered** and **flexible** nanostructures over **large area**
- Morphological manipulation for hot spots
- Metrological evaluation of the **substrate efficiency**
 - enhancement factor: traceable calibrated RF-XRF for **molecule quantification**



Cara, E. et al. Nanomaterials, **2020**, 10 (2), 280



FINAL REMARKS

- Self-assembly-based fabrication: **long-range-ordered** and **flexible** nanostructures over **large area**
- Morphological manipulation for hot spots
- Metrological evaluation of the **substrate efficiency**
 - enhancement factor: traceable calibrated RF-XRF for **molecule quantification**



TAKE-HOME MESSAGE

- Aim for **reproducibility** in experiment through standardisation of the **fabrication protocol**.
- Allow **comparison** with other laboratories through clear description of assumptions and **methods**.

FINAL REMARKS

- Self-assembly-based fabrication: **long-range-ordered** and **flexible** nanostructures over **large area**
- Morphological manipulation for hot spots
- Metrological evaluation of the **substrate efficiency**
 - enhancement factor: traceable calibrated RF-XRF for **molecule quantification**



TAKE-HOME MESSAGE

ACS NANO



Cite This: ACS Nano 2019, 13, 4862–4864

www.acsnano.org

Redefining the Experimental and Methods Sections

ACKNOWLEDGEMENTS



Nanofab

N. De Leo



E. Cara



F. Ferrarese
Lupi



A. Giovannozzi

AFM



F. Celegato



L. Mandrile

A. Sacco
A. M. Rossi



L. Boarino



R. Rocci



M. Fretto



I. Murataj

SERS



AFM



F. Celegato

Synthesis and simulations



B. Beckhoff

EMPIR



K. Sarnacci



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

The projects **I5HLT01**,
MetVBadBugs and **I6ENV07**,
AeroMet have received funding from the EMPIR PROGRAMME.



ACKNOWLEDGEMENTS



Nanofab

N. De Leo



E. Cara



A. Giovannozzi



SERS



L. Mandrile

A. Sacco
A. M. Rossi



F. Celegato

AFM



L. Boarino



F. Ferrarese
Lupi



M. Fretto



P. Hönicke

XRF



I. Murataj

Synthesis and simulations



Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin



B. Beckhoff



M. Laus
M. Cossi
D. Marchi
A. Zoccante



K. Sarnacci

e.cara@inrim.it

Comments!

Questions?

Ideas ...