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# UV and THz assisted APT analysis of a silica matrix for bio-particles embedding

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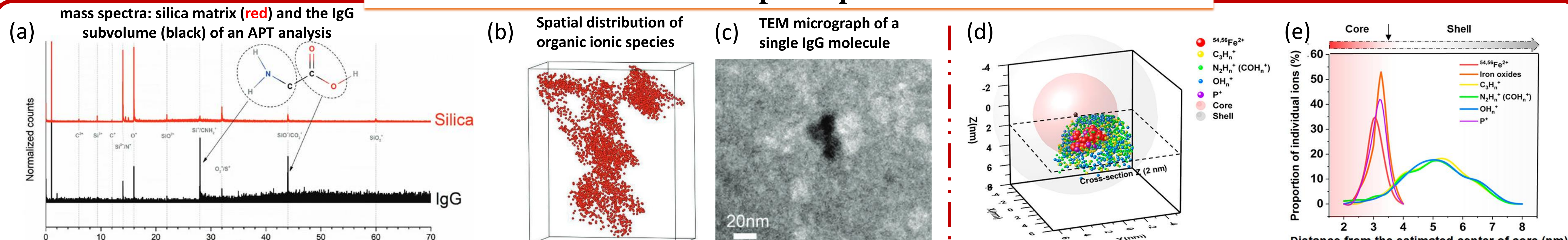
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## Abstract

Unravelling the 3D structure and composition of biological macromolecules at nanoscale sheds light on their functions and interactions. In such a context, **Atom Probe Tomography (APT)** is lately arousing interest because it provides a three-dimensional compositional mapping with sub-nanometric resolution, adding high chemical sensitivity throughout the whole periodic table of elements [1]. Recently, it has been shown that biomolecules can be embedded in dielectric materials, such as silica, and analyzed by the **laser-assisted APT (La-APT)**, by combining the actions of a high DC field and an ultrashort laser pulse [2]. In this work, we focus on the APT analysis of **amorphous silica matrices embedding ferritin proteins**, synthesized via a water glass sol-gel process, with the aim to recreate a viable environment for biomolecules [3]. Three different APT analyses are compared, differing for laser illumination configurations: a La-APT shining UV radiation (**LAWATAP**) and a Terahertz-assisted APT (**Tera-SAT**), providing a mono-cycle THz high field.

## Laser-assisted APT of biosamples – previous remarkable results



[3] A method for **IgG protein encapsulation in an amorphous solid silica matrix**, called **water glass via sol-gel process**, is described. Dominant amino-acid traces ( $\text{CNH}_2^+$ ,  $\text{CO}_2^+$ ), are recognizable in IgG mass spectrum (a) and are spatially reconstructed by generating an iso-density region with a specific filtering criterion (b). Bright field transmission electron microscopy (TEM) confirms “Y-shaped” IgG monomers were encapsulated inside the silica matrix (c).

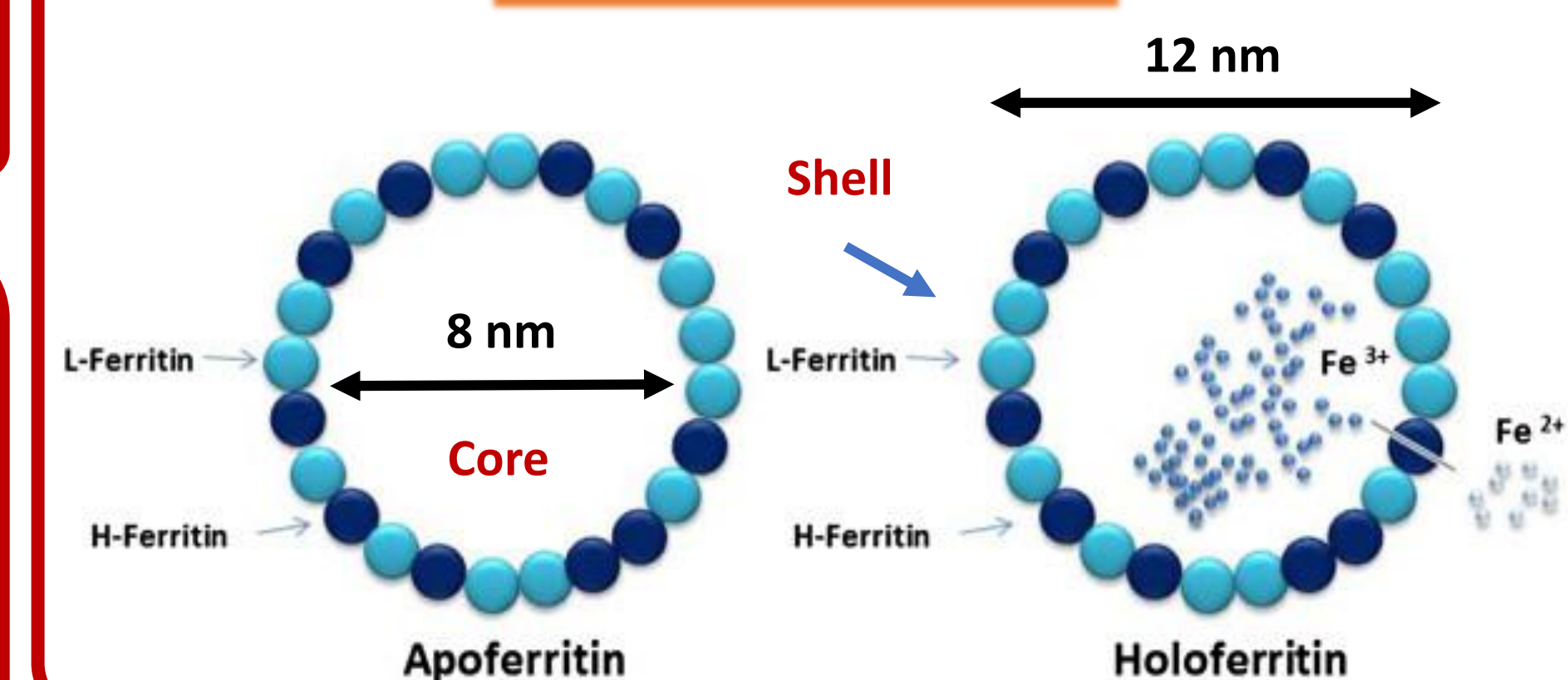
[4] APT analysis provides the composition and the distribution of iron atoms in the core of **ferritin** (d), an iron-storing protein.  $^{54,56}\text{Fe}^{2+}$  is densely located at the inner core,  $\text{P}^+$  in both the inner core and core/shell interface and iron oxides are mostly distributed at the core/shell interface (e).

## Tasks

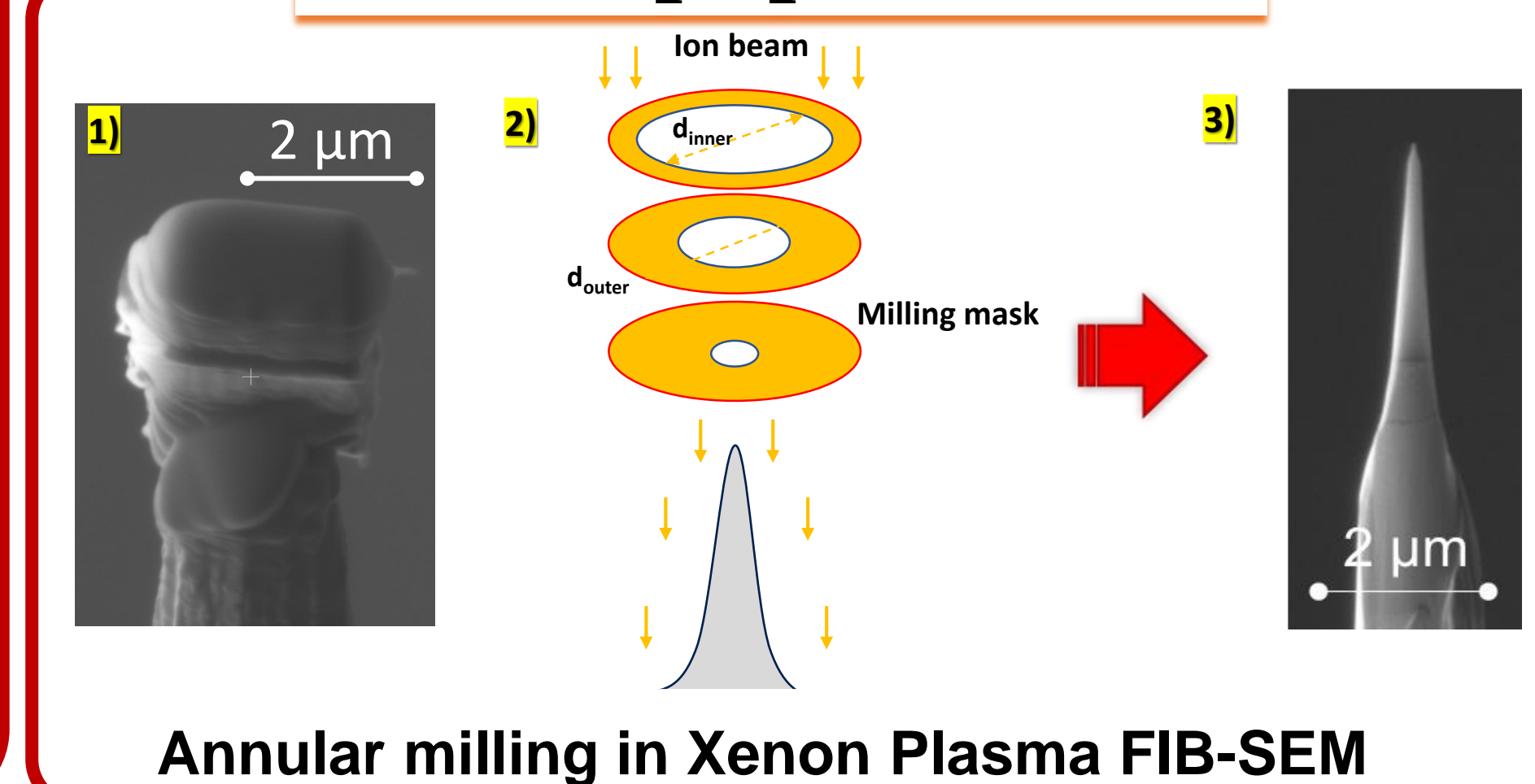
- ❖ Amorphous silica matrix synthesis via water glass sol-gel process
- ❖ Nanometric needle shaped tips production by Focused Ion Beam (FIB)

- ❖ Test on a small biological structure (**ferritin protein**)
- ❖ APT analysis on LAWATAP (UV-laser APT) and Tera-SAT (THz-APT)

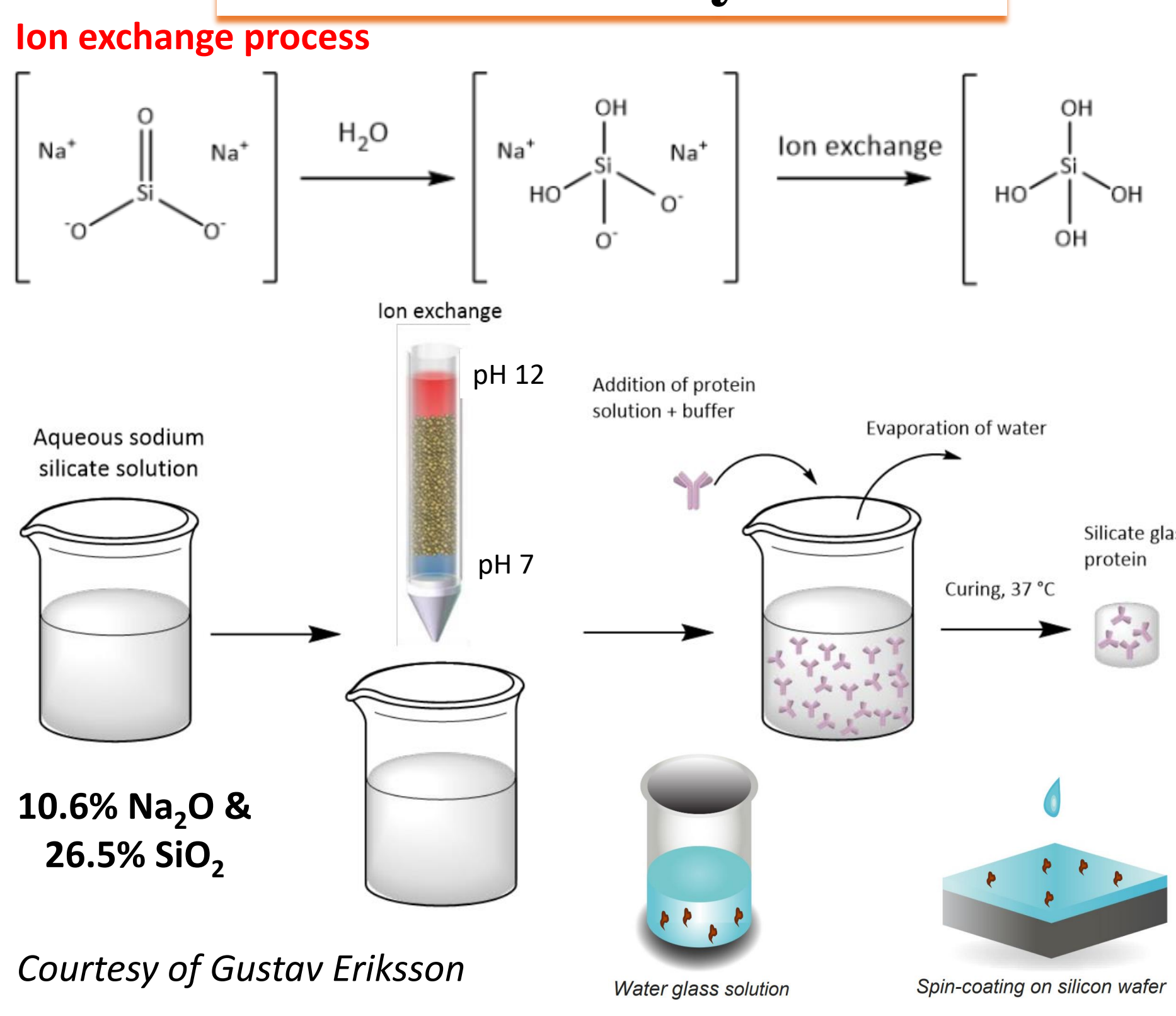
## Ferritin structure [5]



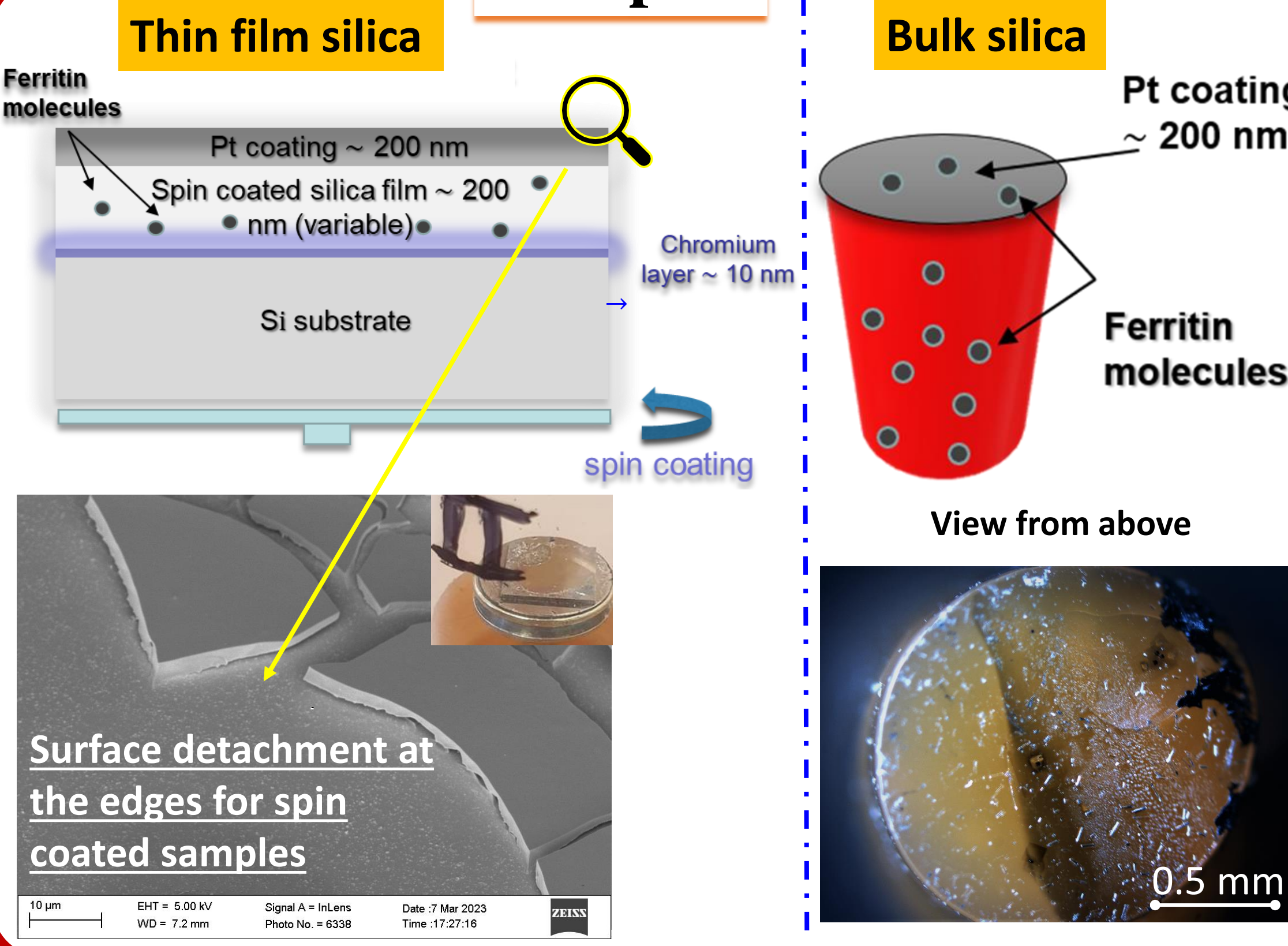
## Nano-tips production



## Silica matrix synthesis



## Samples

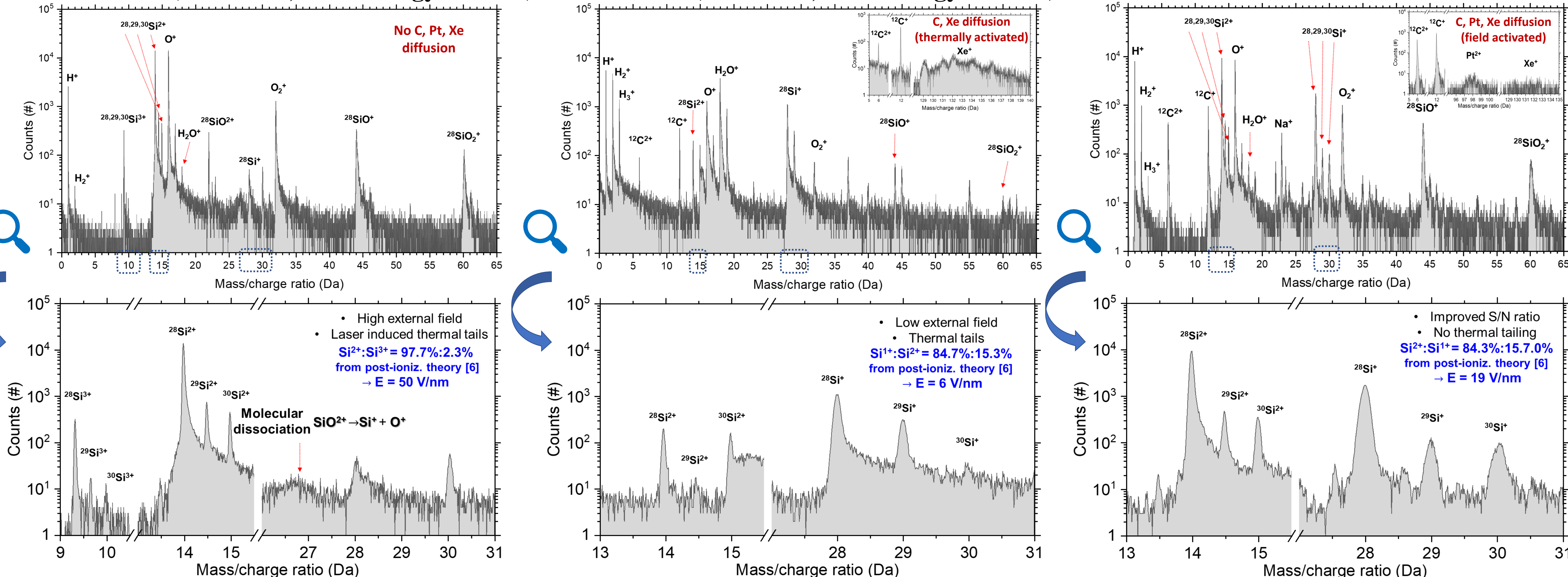


## Results – APT mass spectra (300 kilo atoms)

### LAWATAP ( $\lambda=343$ nm, laser energy = 25 nJ)

### LAWATAP ( $\lambda=343$ nm, laser energy = 32 nJ)

### THz

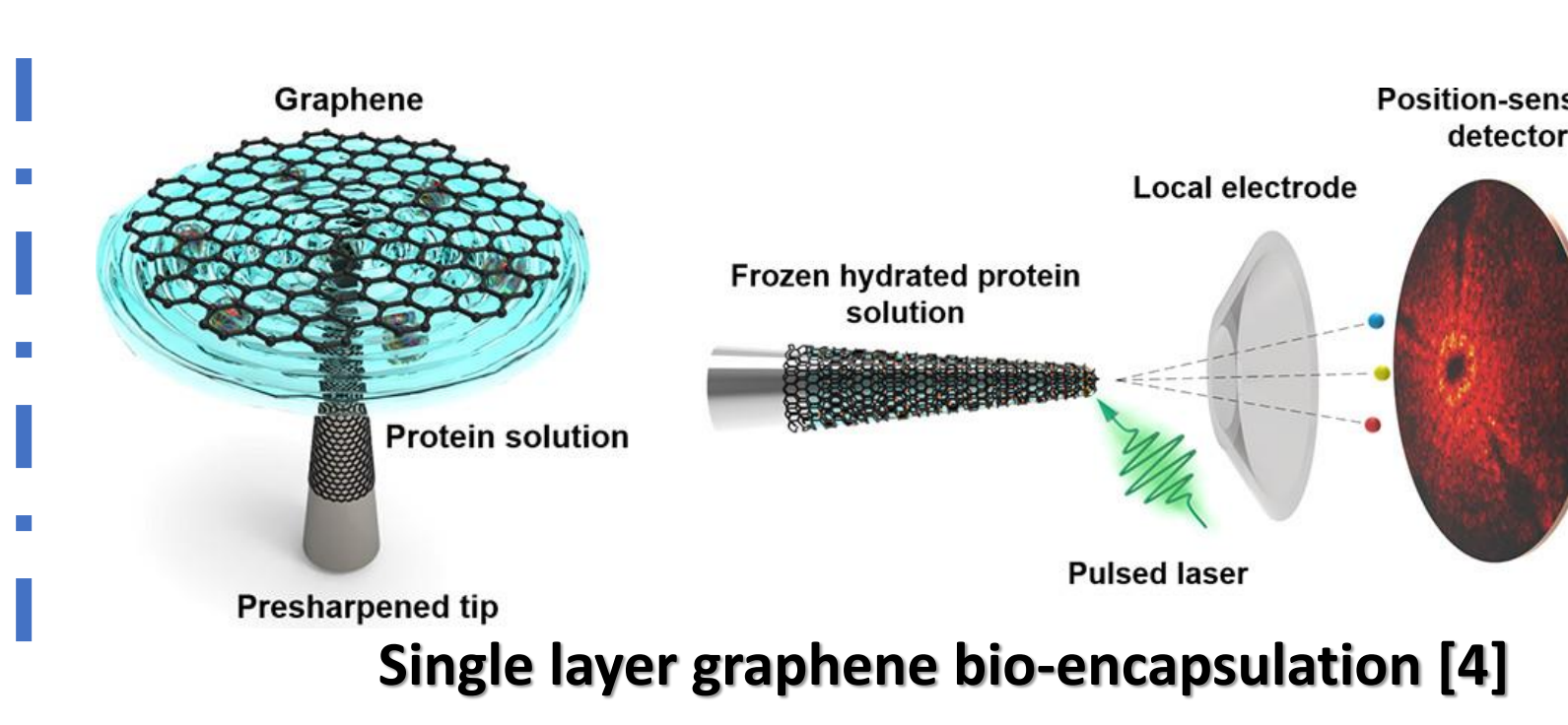


## Conclusions and perspectives

- ✓ **Analysis of silica matrix in laser APT is possible**
  - ❑ Better results at lower laser energy and high static field in UV
    - better signal-to-noise ratio
    - Absence of Carbon diffusion
  - ❑ Difficult protein-related peaks detectability
    - ❑ No reliable protein-related atom species quantification
      - overlaps with matrix peaks (ex.  $^{56}\text{Fe}^{2+}$  and  $^{28}\text{Si}^+$ )
    - ❑ Small analysis volume in THz setup
      - Low repetition rate (1 kHz)
- ❑ Reduction of thermal effects in THz
  - Good signal-to-noise ratio (comparable to UV-assisted)

Test THz in higher field conditions

Improve S/N ratio and mass resolution compared to UV



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