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Wine sulphites sensing by Surface-Enhanced Raman Spectroscopy

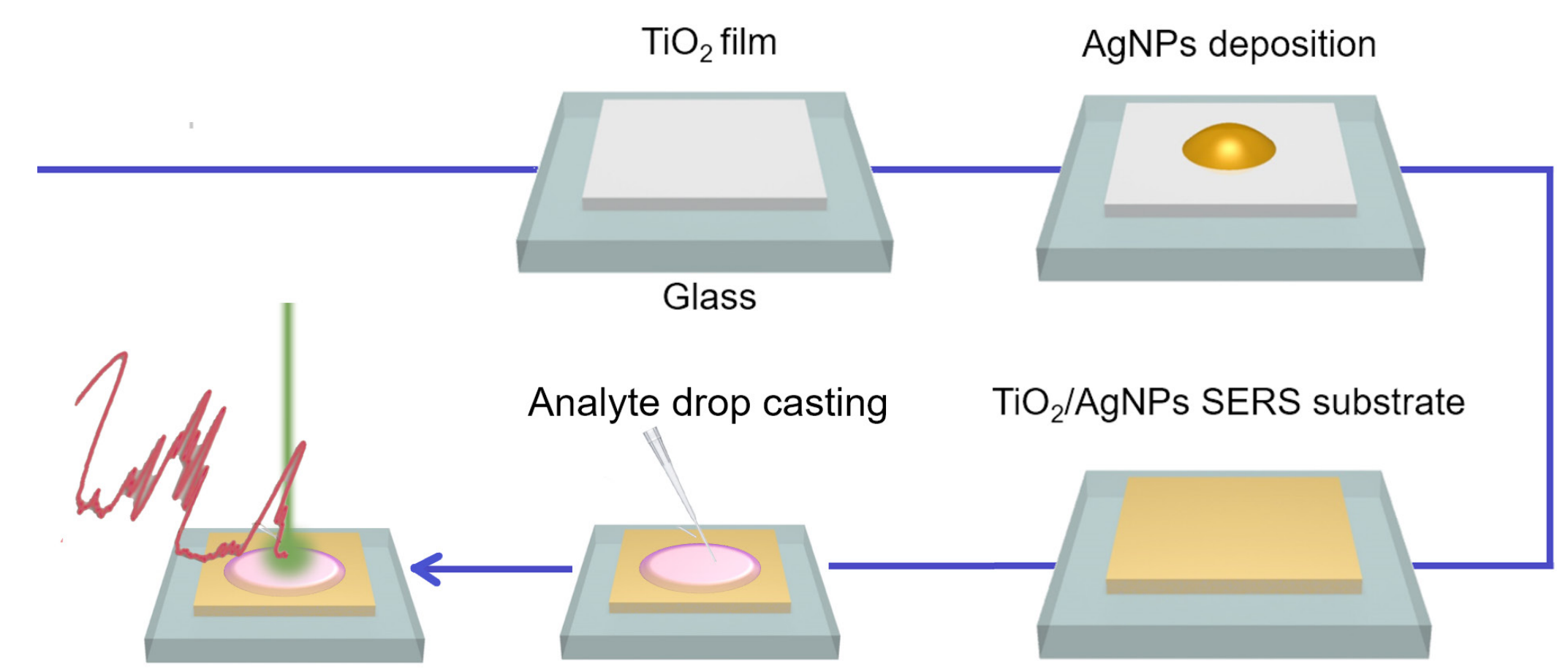
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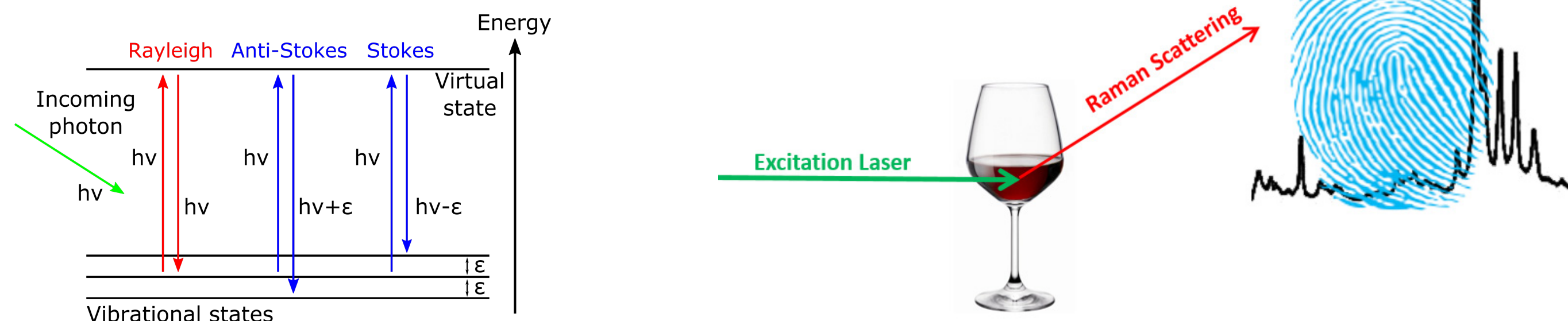
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Sulphur dioxide (SO₂) is widely used as an antimicrobial and antioxidant agent in winemaking [1]. However, sulphites are considered toxic to human health [2], and legal limits have been established via EU Regulations [3] to guarantee a safe use of sulphites for human consumption. Currently, SO₂ content in wines is analysed by volumetric analysis, using acid-base or redox titrations, by the designated control laboratories.

In the present contribution, a simple and inexpensive sensor to detect and quantify sulphites in wine is proposed. A dedicated Surface Enhanced Raman Spectroscopy (SERS) substrate for this specific application was developed and optimised. SERS is a non-destructive and ultrasensitive molecular spectroscopy technique, exploiting the plasmonic physics of nanostructured metals [4]. Plasmonic nanoparticles (NPs) have raised great interest in the field of chemical and biological sensing, thanks to their ability to increase the intensity of Raman signals of molecules in proximity of their surfaces. Moreover, this technique allows fast collection time and highly specific label-free analysis due to the molecular fingerprint provided by Raman spectra. In addition, several calibration strategies can be applied to obtain quantitative information.

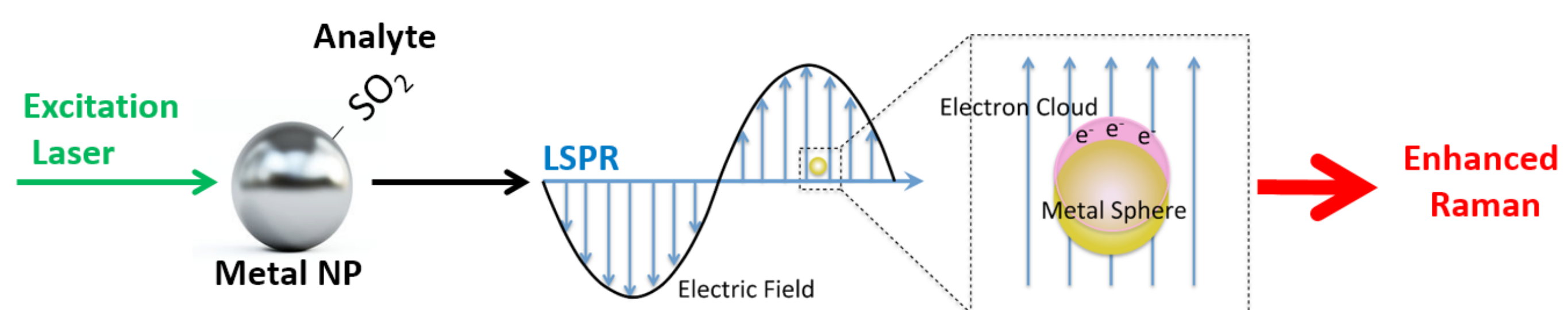


The principle of SERS

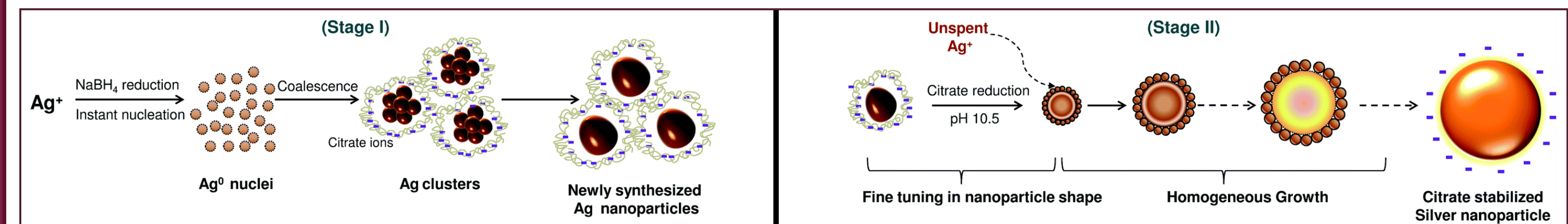


The frequencies of Raman scattered photons bring specific chemical information about the sample. Raman spectroscopy belongs to untargeted fingerprint technologies. This technique can be used for compositional sensing based on the specificity of the pattern of signals present in the Raman spectrum. Quantitative information can be obtained, after calibration, based on the Beer-like correlation between intensity and amount of substance.

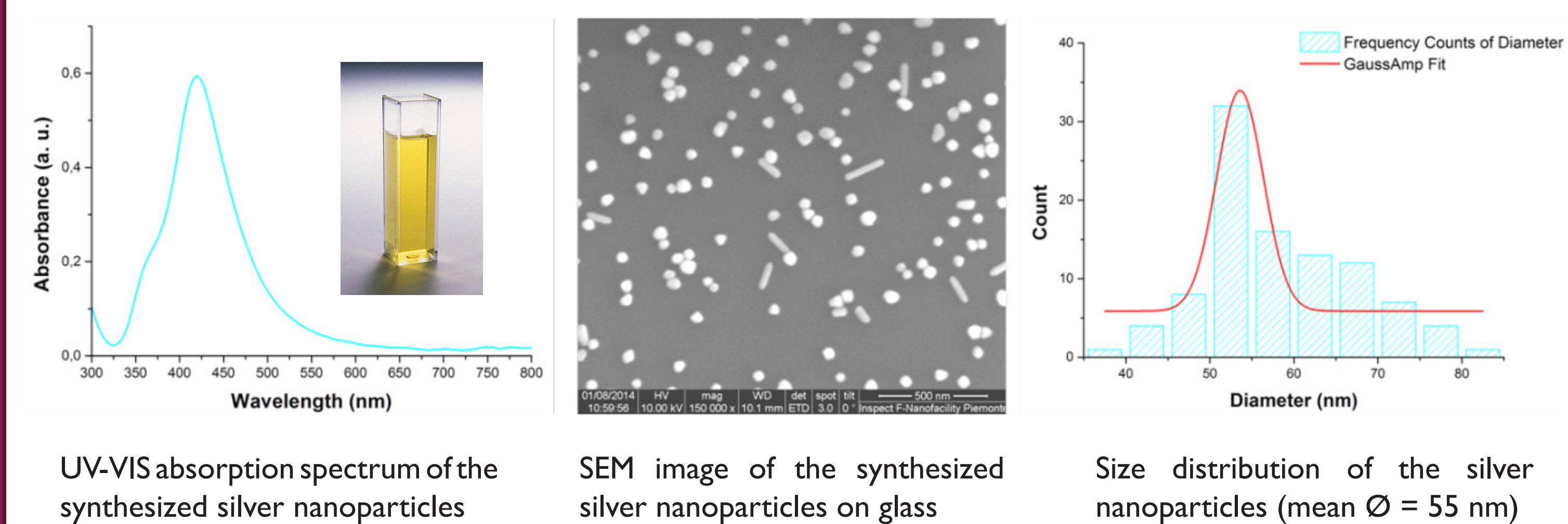
Surface Enhanced Raman Scattering represents a strategy to increase the sensitivity of Raman. When plasmonically active nanomaterials are invested by the laser, a local increase of the electromagnetic field is registered. HOT SPOTS are generated in proximity of metal nanostructures surfaces and the Raman signals of molecules located into the hotspots are intensified.



SERS-active silver nanoparticles - Synthesis

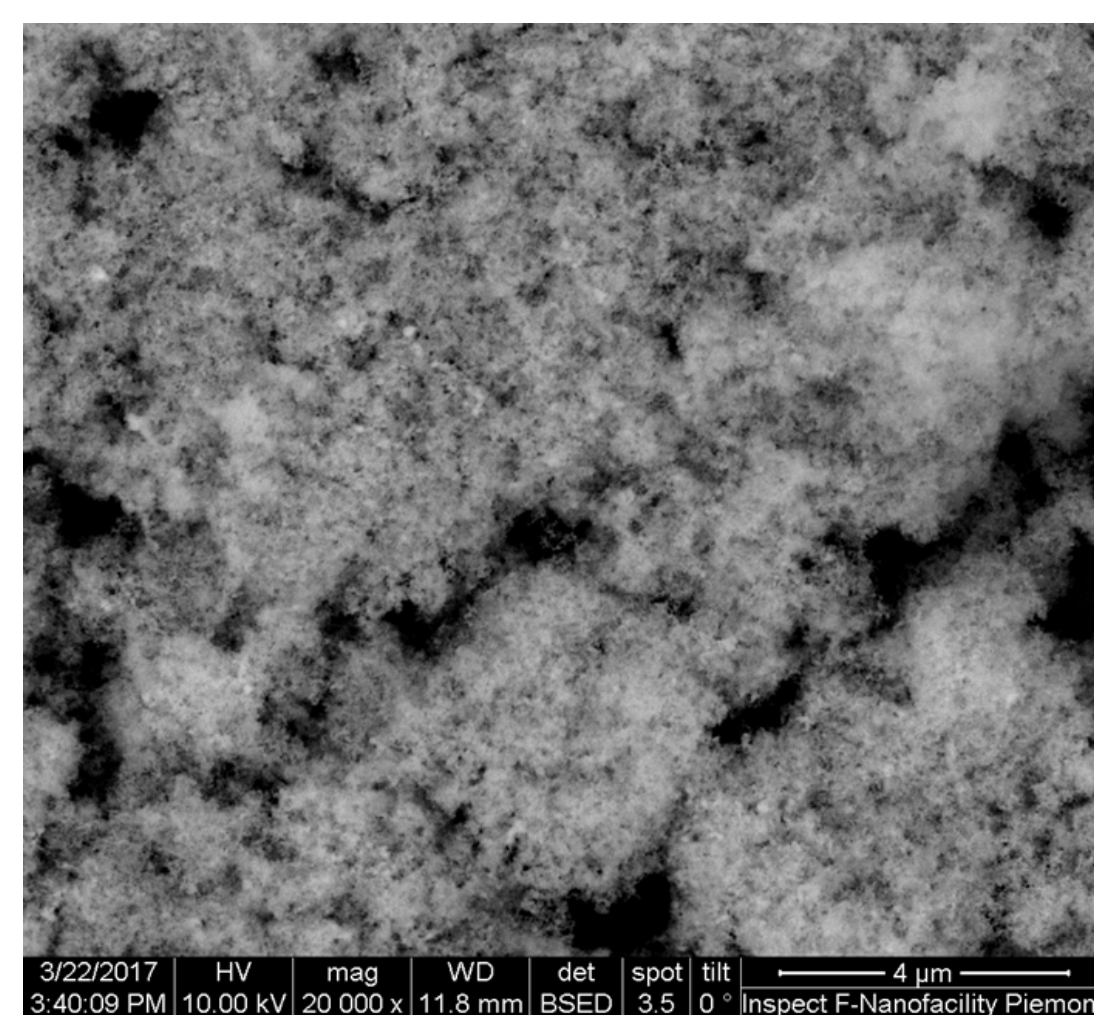
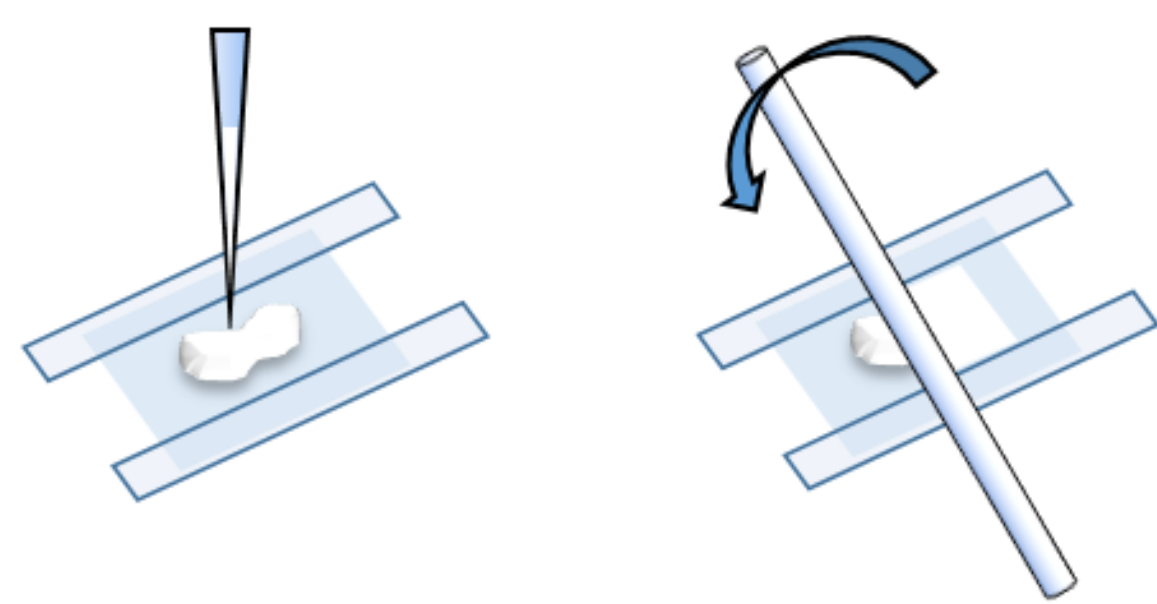


AgNPs characterization



The SERS sensor preparation procedure

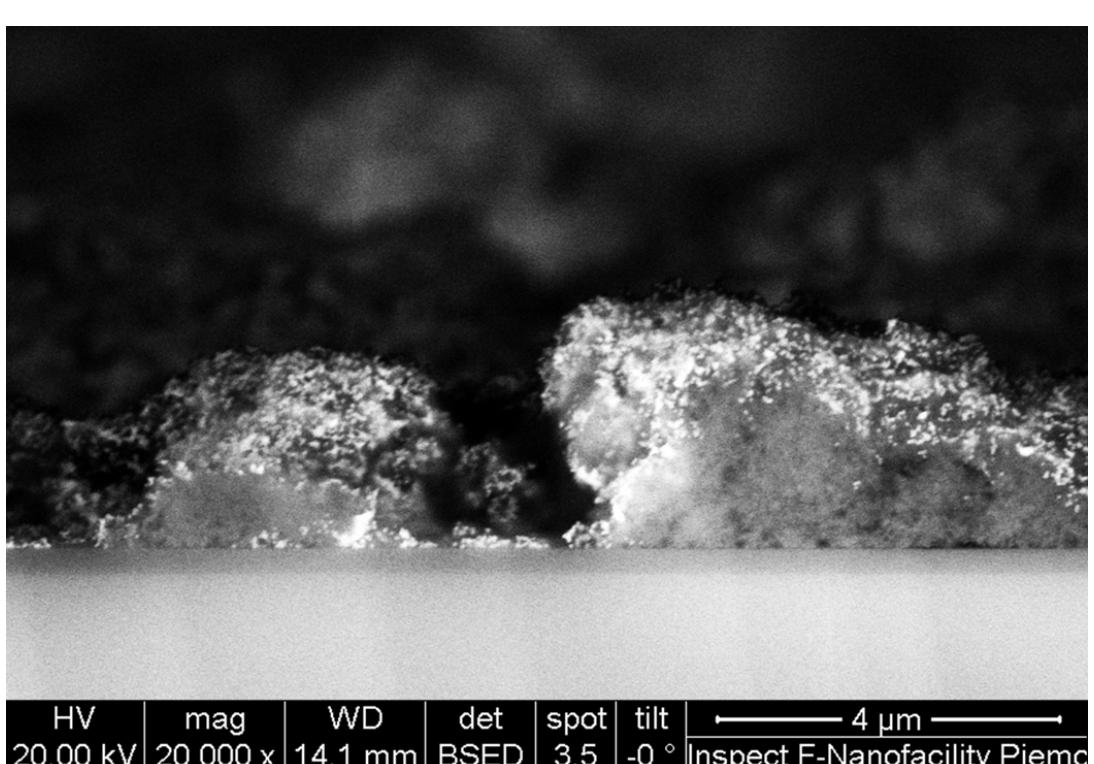
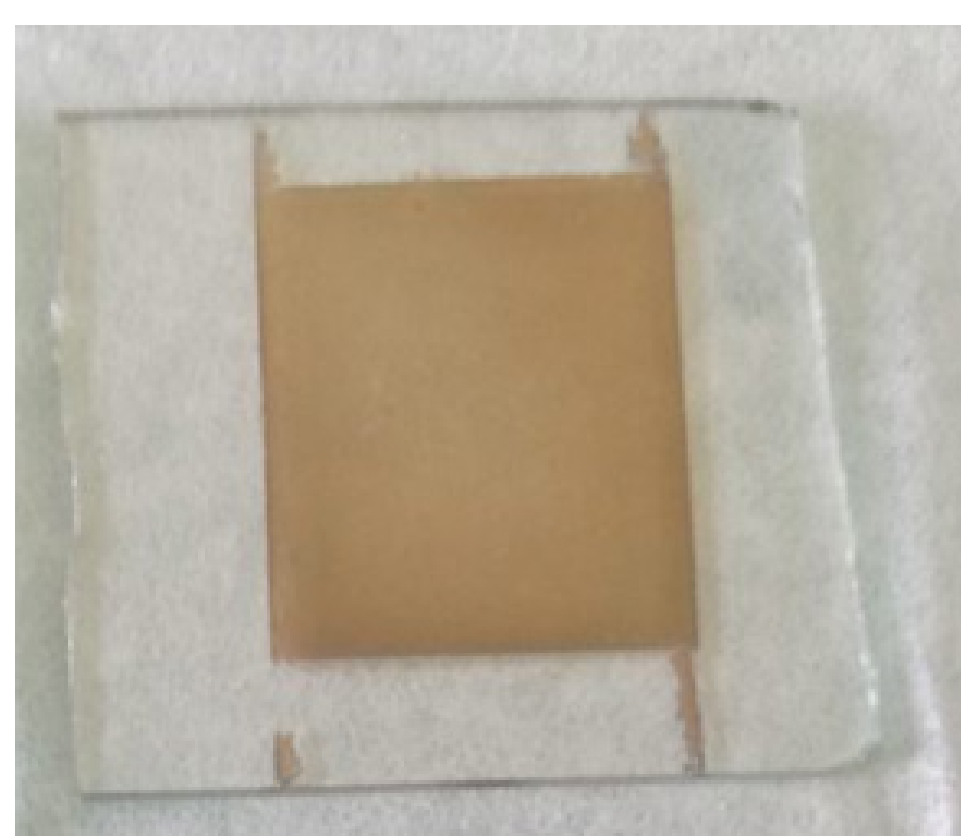
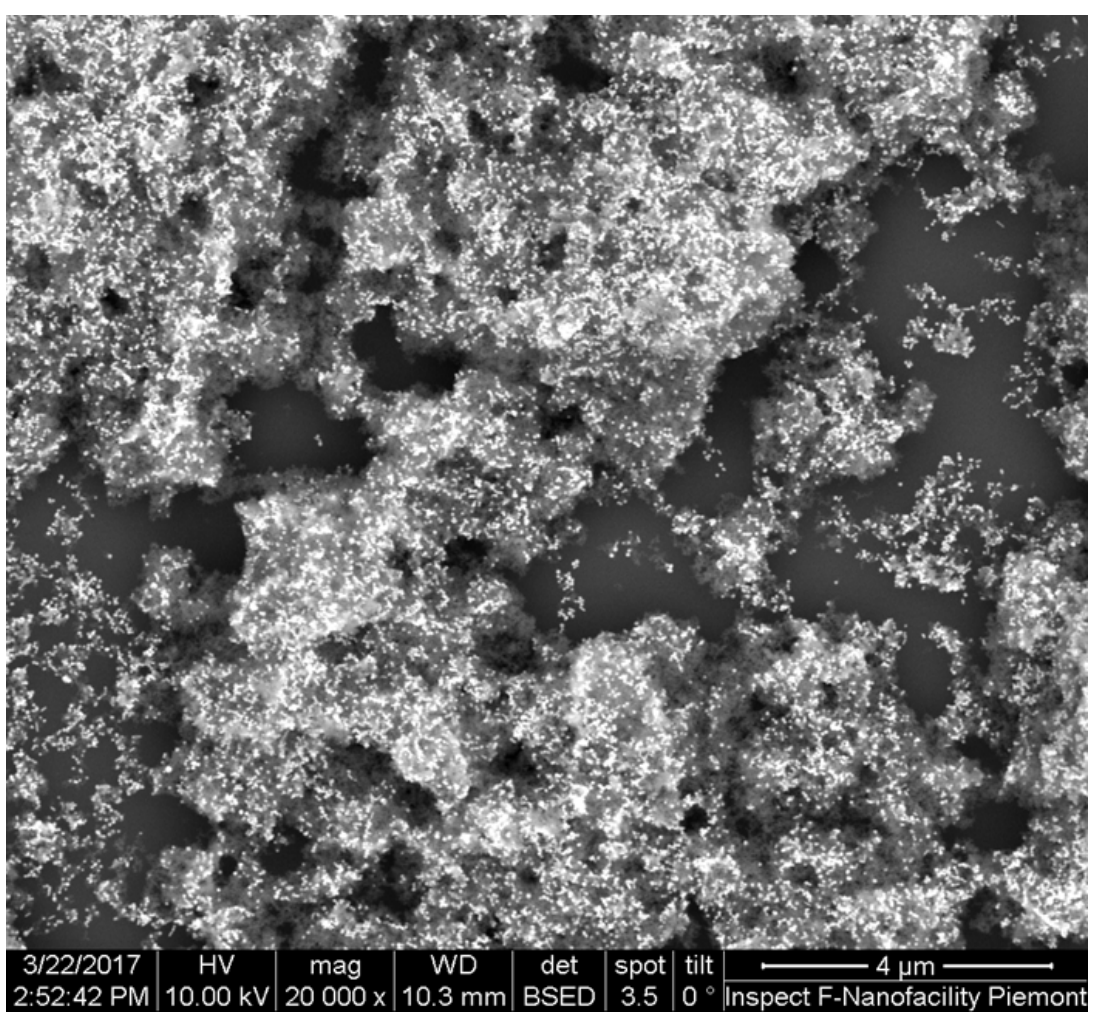
1. TiO₂ deposition
2. Doctor Blade spread



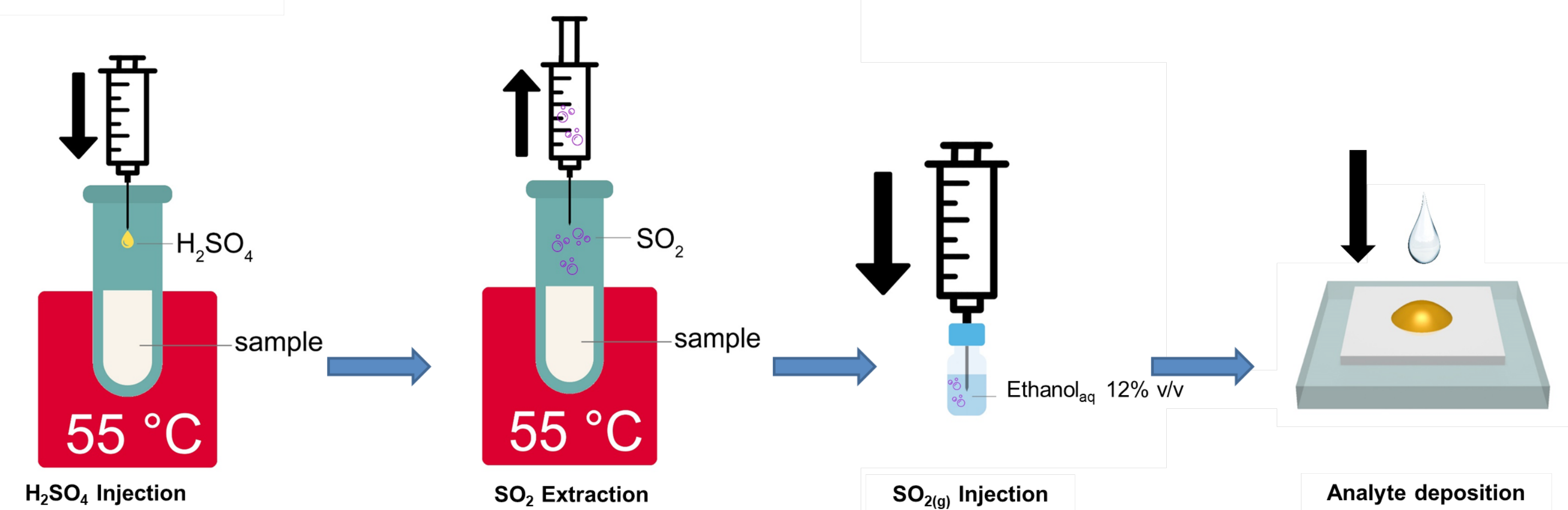
The fabrication procedure is schematically represented above. P25 TiO₂ paste 10% w/w in ethanol is prepared and homogenized in ultra-sonic bath at 15°C and at a power of 80 W to obtain stable and well de-agglomerated nanoparticles. A thin porous film on glass substrate is obtained using a glass stick as a rolling pin by manual Doctor blade deposition, with the help of a mask defining an area of 1 cm².

AgNPs colloids, previously synthesized are concentrated and re-dispersed in EtOH by centrifugation (10 min, 3000 rpm). 10 µl of concentrated AuNPs/EtOH are dropped on the TiO₂ square pad. The AuNPs diffuse through the pores and micro-channels of the titanium dioxide layer and EtOH evaporates very rapidly provoking a uniform covering of the surface.

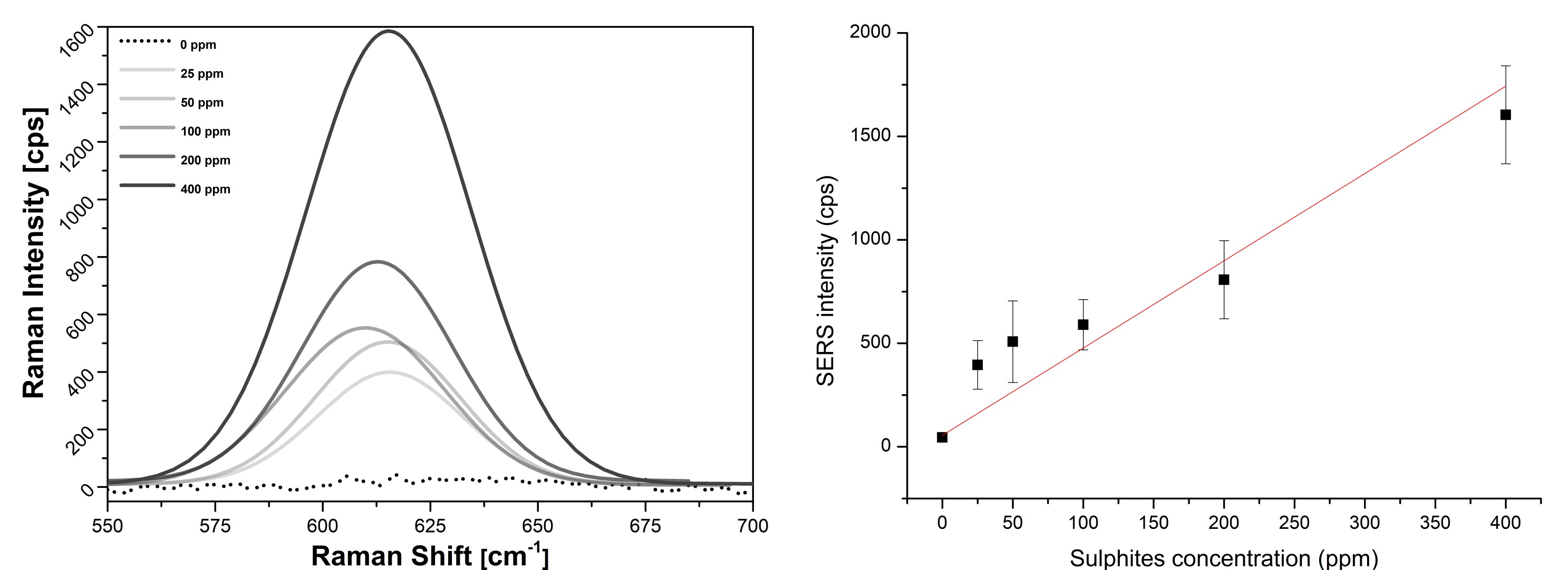
3. AuNPs deposition
4. Solvent evaporation



The application tests



Head Space Gas Extraction is performed to avoid undesired matrix effect revealed during direct drop deposition tests. The wine sample is acidified with sulfuric acid to release SO₂ vapours in the head space chamber. The released gas is re-injected and solubilized into a hydroalcoholic solution (12% v/v), then dropped on the SERS sensor. The high binding affinity between AgNPs and sulphite species (SO₂, HSO₃⁻, SO₃²⁻) is responsible for the intense SERS response. The specific S-O bending vibrational mode signal at 615 cm⁻¹ on the SERS spectra can be monitored to obtain quantitative information. Samples with increasing concentration of sulphites from 25 ppm up to 400 ppm were analyzed. A linear correlation between SERS intensity of sulphite related bands was determined.



Conclusions and future perspectives

In conclusion, SERS-active composite films were prepared by TiO₂-mediated deposition of AgNPs on glass. The sensor was positively tested in the concentration range from 25 to 400 ppm, in compliance with the detection limits requested by the law in vigour, for both red and white wines. The preparation of the proposed SERS sensor is rapid, simple, and inexpensive. HG-GE SERS measurements take less than two minutes, which is highly desired in routine analysis labs. Matrix effects are negligible, and adequate sensitivity was reached for the application.

The whole uncertainty budget of the method, the recovery efficiency, and the stability of the sensor response will be studied to improve quantification results, in terms of accuracy and precision. After the method optimisation, a metrological comparison between the sensor performances and the official methodology currently in use in routine control laboratories will be needed to drive this technique to real application level.

References:

- [1] P. Ribereau-Gayon, et al., Handbook of enology: The microbiology of wine and vinifications (2006, 2nd ed., Wiley).
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- [4] R. Aroca, Surface-Enhanced Raman Scattering, Surface-Enhanced Vibrational Spectroscopy (2006, John Wiley & Sons).

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