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SERS Substrates for Sensitive Molecular Detection

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Introduction

Surface Enhanced Raman Spectroscopy (SERS) is a surface-sensitive technique that strongly enhances the Raman signal of molecules absorbed on the surface of metal nanoparticles.

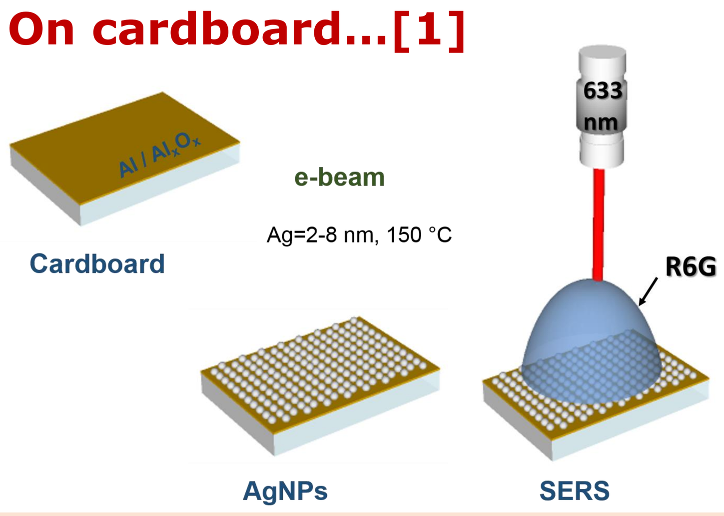
At CENIMAT/i3N we are investigating the fabrication of silver nanoparticle (NP) plasmonic SERS surfaces grown by physical dewetting method and by chemical synthesis (in collaboration with the group of R. Franco, UCIBIO-FCT-NOVA and E. Pereira, ICETA-FCUP) on different types of substrates: silicon, glass, Tetrapack and paper.

The dewetting growth of Ag NPs on silicon and tetrapack substrates allows the formation of closed packed arrays of NPs with a controlled size of 60 nm that provides an enhancement of the Raman signal, designed by Enhancement Factor (EF) of up to 10^6, in a uniform and reproducible way [1]. On the other hand, paper substrates coated ZnO nanorods decorated with Ag NPs [2] or with silver nanostars allows to obtain uniform SERS substrates with EF of 10^7, a state of the art results for paper SERS substrates.

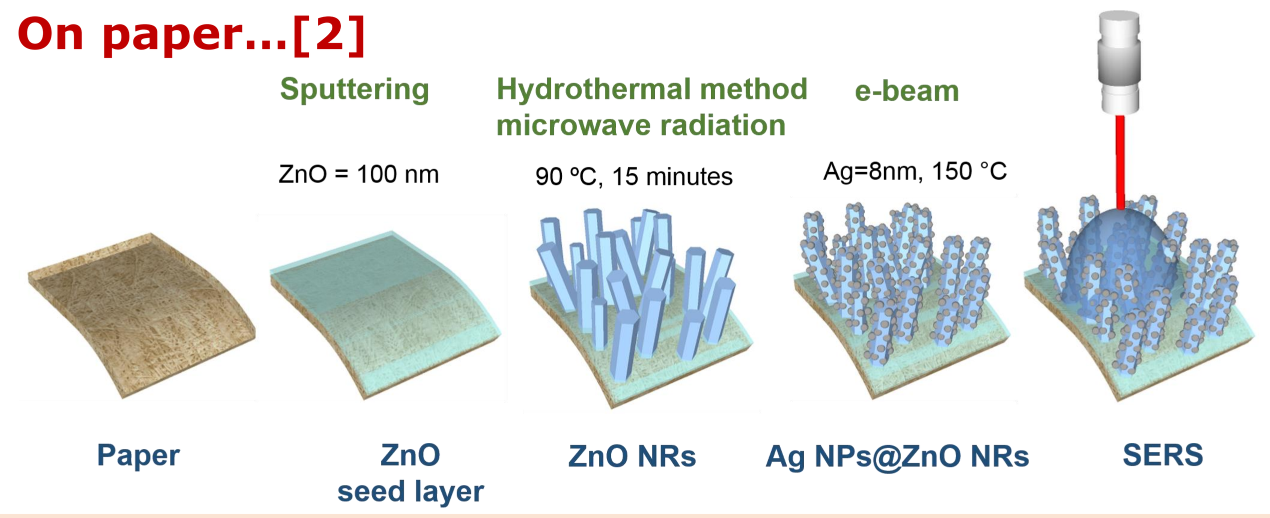
A recent FCT funded project – DISERTOX aims to combine these SERS substrates with microfluidics to concentrate toxins and pesticides at the detection spot allowing to determine concentrations at sub ppb range, using low cost uniform efficient platforms.

Experimental Section

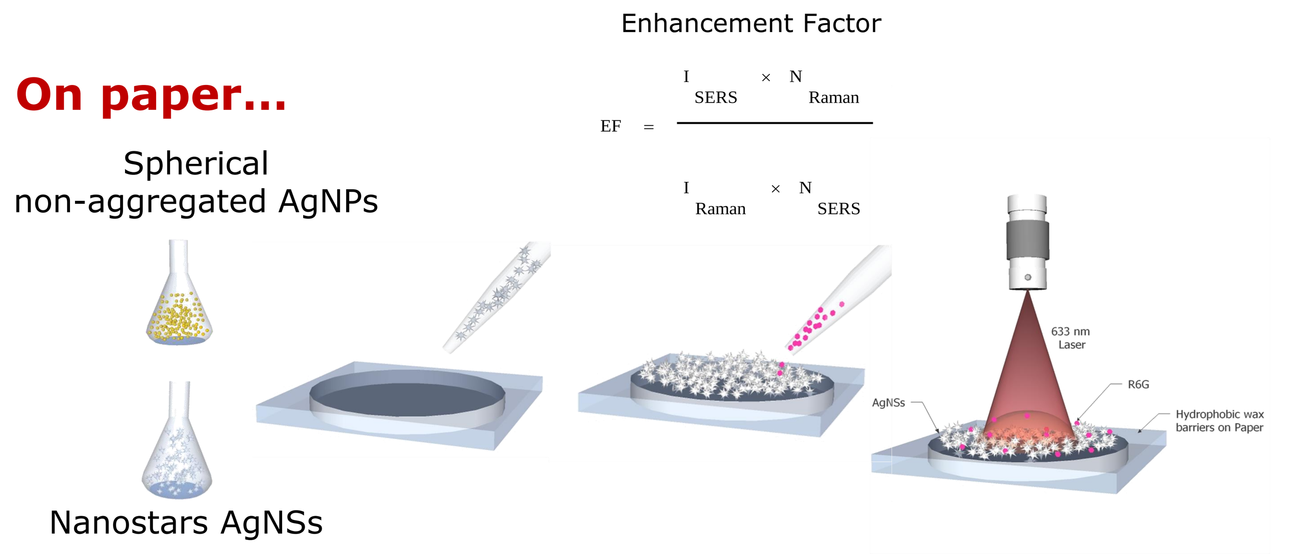
On cardboard...[1]



On paper...[2]

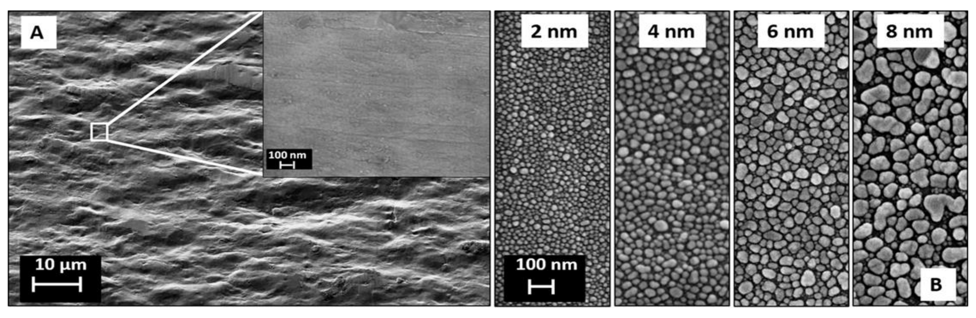


On paper...



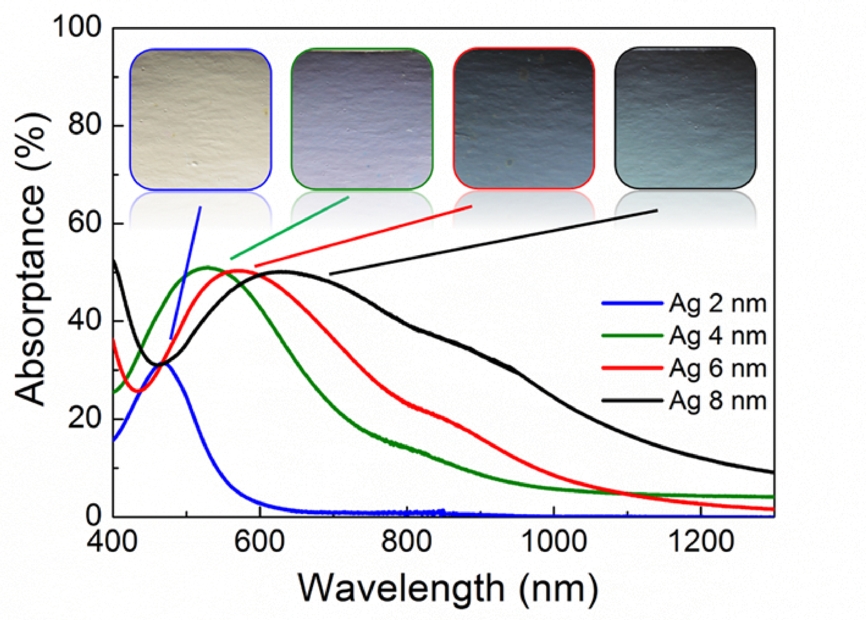
Results and Discussion

Nanoplasmonic Cardboard Substrate



- mass thicknesses increases → elongated shape larger in size

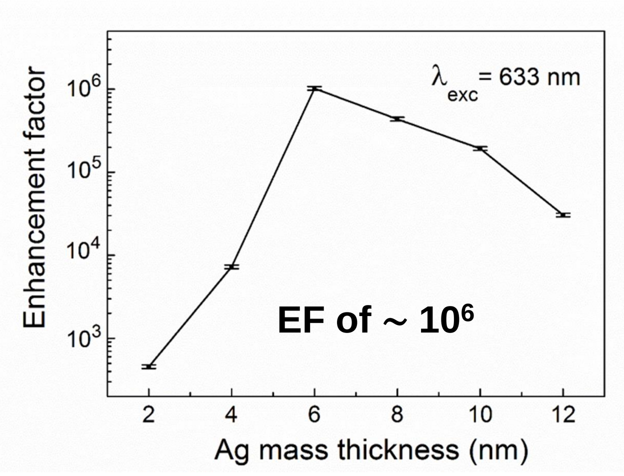
Optical characterization and Raman measurements



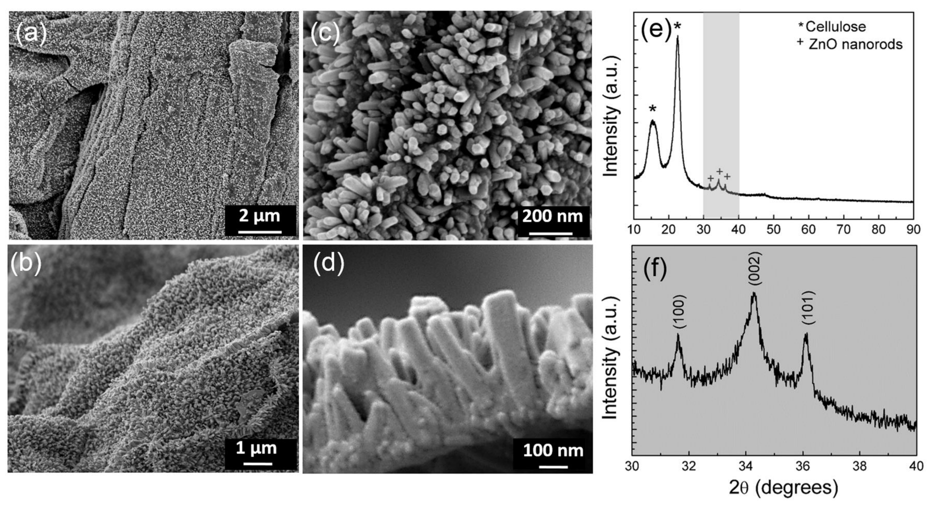
- Increase of the Ag mass thickness leads to an:
  increase in the average particle size
  more elongated semi-ellipsoidal shapes

red shift and broadening of the LSPR peaks

SERS properties



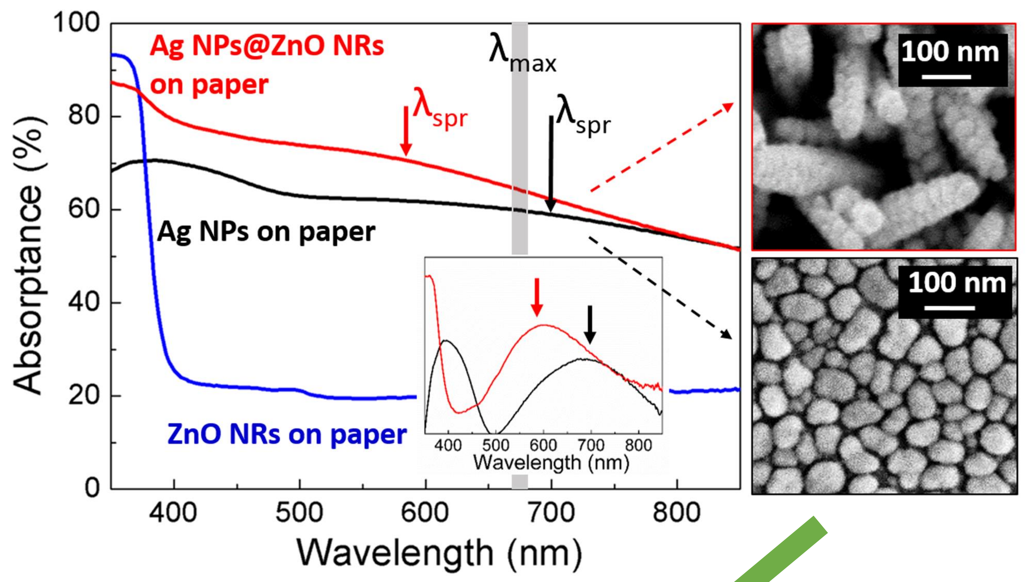
Plasmonic ZnO nanorods on paper substrate



Quasi-aligned Hexagonal NRs

Width
50–100 nm

Length
200-300 nm



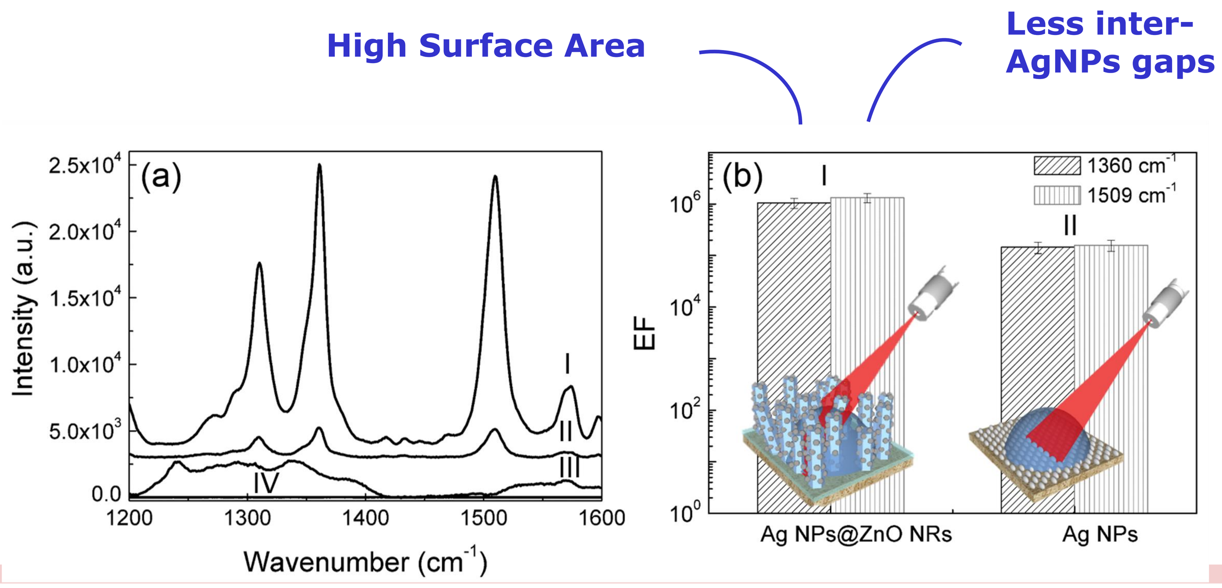
Paper / NPs
NPs 50-80 nm, separation of less than 10 nm

Paper / ZnO / NPs
NPs 30-40 nm, separation of less than 5 nm

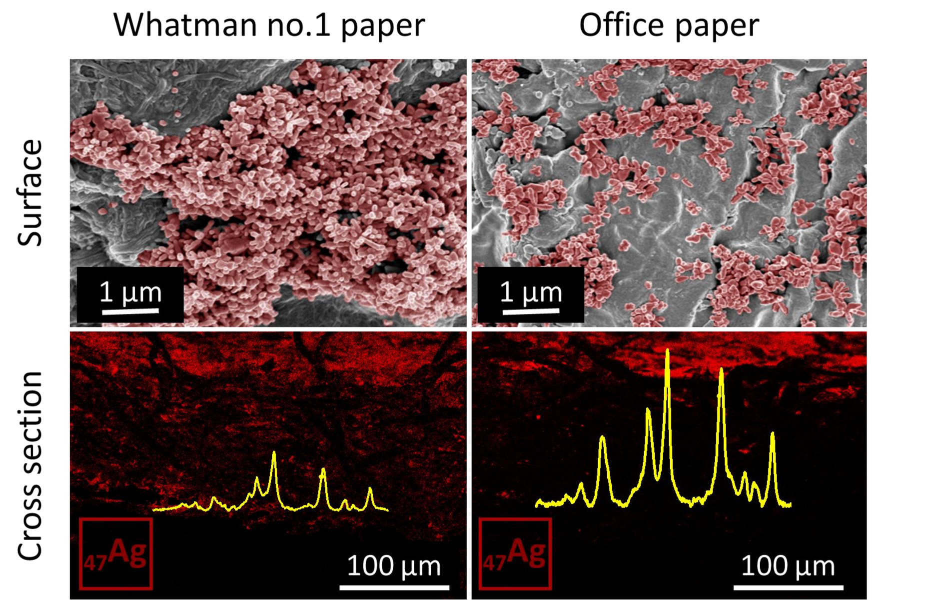
SERS properties

High Surface Area

Less inter-AgNPs gaps

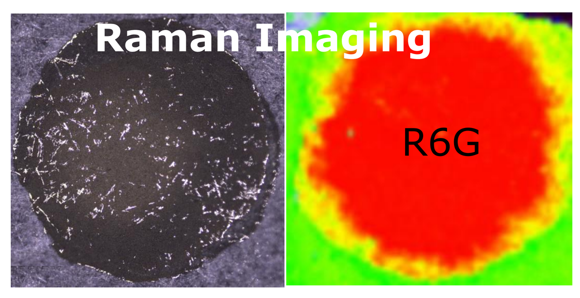


Development of paper SERS substrate

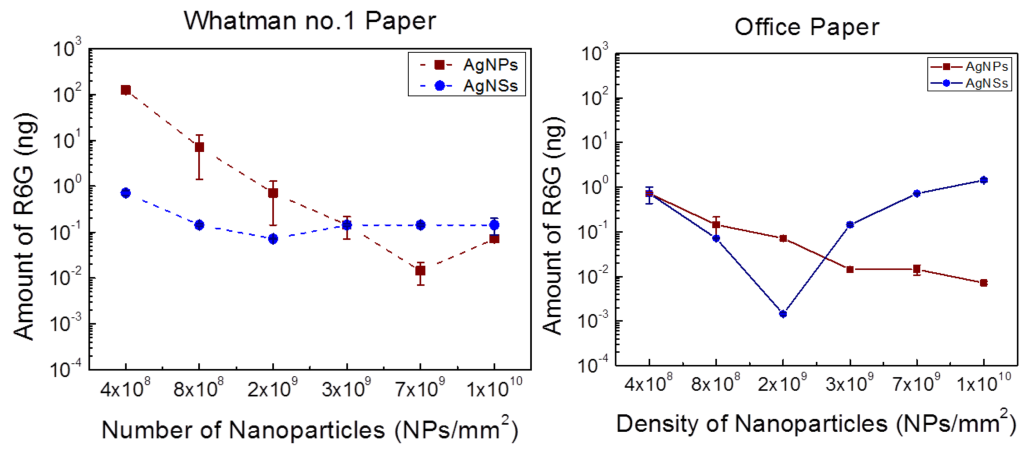


- AgNSs were distributed through the entire thickness of Whatman paper
- AgNSs added to the office paper were observed practically only retained on the surface of paper fibers.

Distribution of R6G in the paper SERS substrate



Paper SERS substrates assays



LOD	LOQ
11.4±0.2 pg	34±7 pg

EF
(3.0±0.7)x10^7 for 10^{-9} M

Conclusions

Cost-efficient, mechanically-bendable, uniform and stable SERS substrates have been developed at CENIMAT/i3N using paper as the base platform. Success has been achieved following 3 different approaches: Ag NPs grown by dewetting in aluminum coated paper cardboard; ZnO nanorods grown on paper and decorated with Ag NPs grown by dewetting; and well patterned office paper covered with Ag nanostarts dropcasted. EFs of 10^7 and LOD of $9x10^{-9}$ ng of R6G have been achieved. These substrates have proved to be have the ideal structure for the development of a SERS sensing systems that are recyclable, flexible, lightweight, portable, biocompatible and economically cheap.

References

[1] Araújo A, at al. Nantechnology, 25 (2014) 415202.
[2] Araújo A, at al. Flex. Print. Electronics, 2 (2017) 014001

Acknowledgments

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