Nanotrenches-based flexible platform for surface-enhanced Raman scattering trace level detection

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We report the development of highly sensitive substrates as surface-enhanced Raman scattering (SERS) spectroscopy detection platforms consisting of nanoimprint lithography (NIL) fabricated plastic nanotrenches covered by nanostructured silver (Ag) films with thicknesses of 10 nm, 25 nm, 50 nm and 100 nm deposited by direct current (DC) sputtering. The morphological and structural properties of the metalized nanotrenches were assessed by scanning electron microscopy (SEM) technique. Crystal violet (CV) was used as analyte to test the SERS activity of the substrates with or without the nanopatterns. We assessed the SERS enhancement activity from the synergy of three key aspects: the Ag metallization, the effect of increasing the Ag film thickness and the imprinted periodic nanotrenches. The contribution of the plasmonic nanostructures contained in the Ag films as well as the contribution of the periodical nanopatterned trenches were investigated, as a cumulative effect to the first contribution. The most promising SERS detection platform is the one with a silver layer of 25 nm on top of the periodic nanotrenches. This substrate showed a considerably lower limit of detection (LOD) for SERS, down to 10 pM, much better uniformity as well as more reproducible signals in comparison with the other metallic films.

Experimental details:

I. NIL fabrication of nanotrenches and Ag nanostructuring: *please review poster* **3D metallic nanotrenches arrays fabricated using nanoimprint lithography** *by* **D. Marconi et al.**

II. Characterization methods:

➢ SEM (Hitachi SU-8230) to assess the morphological and structural properties of the metalized nanotrenches.

➢ Raman/SERS: portable i-Raman spectrometer (Metrohm AG, Herisau, Switzerland) equipped with 532 nm laser line (total power of 50 mW) and connected to a BW-TEK optical microscope with a 20× objective.

For each spectrum acquisition times of 3 s for SERS and 10 s for Raman measurements were used.

SEM images of the imprinted nanotrenches-based samples in IPS® substrate

10 nm Ag   25 nm Ag   50 nm Ag   100 nm Ag

SERS spectra of CV on Ag coated plastic substrates in comparison with the SERS spectrum of the blank Ag covered substrate (without nanopatterns)

10 nm Ag   25 nm Ag   50 nm Ag   100 nm Ag
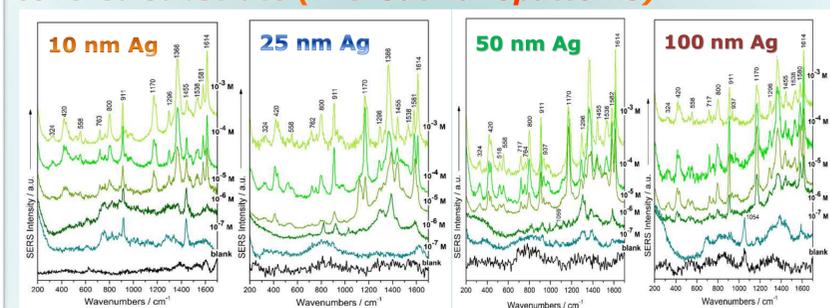
• Suitable SERS detection of CV concentration down to 10^{-5} M using Ag-based plastic substrates without NIL nanopatterns.

SERS spectra of CV on Ag coated plastic substrates in comparison with the SERS spectrum of the blank Ag covered substrate (with nanopatterns)
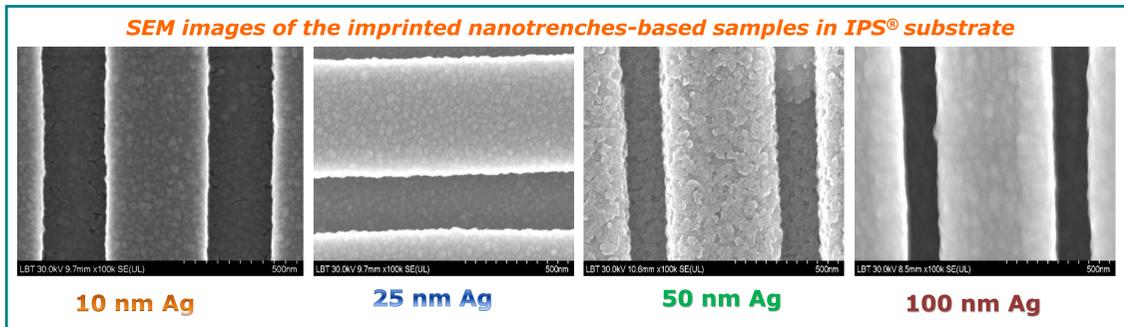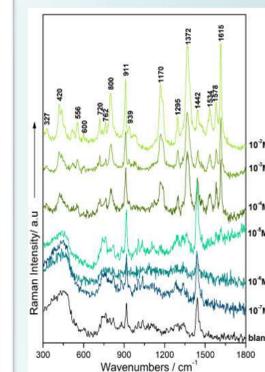

10 nm Ag   25 nm Ag   50 nm Ag   100 nm Ag
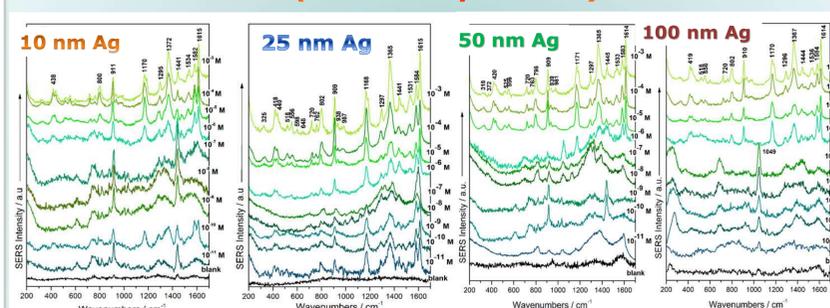
• Suitable SERS detection of CV concentration down to 10^{-11} M using Ag-based plastic substrates imprinted with periodical nanotrenches.

Raman detection of CV on plastic substrate without Ag and the Raman spectrum of blank substrate

Typical Raman bands have been detected as lower as 10^{-4} M concentration of CV:
• intense bands at 1372 cm^{-1} (the phenyl-N stretching) and at 1615 cm^{-1} (benzene stretch);

• medium intensity bands at 800 cm^{-1} (out-of-plane ring C–H bending mode), 911 cm^{-1} (joint contribution from CV - deformations/symmetric stretching/breathing vibration CC atoms in the benzene rings and plastic substrate), 1170 cm^{-1} (stretching vibrations central C atom-N), 1534 cm^{-1} (symmetric deformation in CH$_3$) and 1578 cm^{-1} (benzene deformation).

Enhancement factors and SERS performance of the proposed nanoplatforms

• We took into account the intensity of five marker bands specific to CV.
• The *analytical enhancement factors (AEFs)* were calculated by using the equation proposed by Le Ru *et al.* [E.C. Le Ru et al., J. Phys. Chem. C 111 (2007) 13794-13803].

$$AEF = \frac{I_{SERS}}{c_{SERS}} \times \frac{c_{Raman}}{I_{Raman}}$$

Table 1. The analytical enhancement factor (EF) obtained for each Ag film thickness at the limit of detection (LOD) concentration for CV without periodic nanotrenches pattern, by considering the presence of the main marker bands in the spectral fingerprint.

SERS band (cm^{-1})	Sample thickness (nm)/ SERS LOD (M)				Raman LOD (M)	AEF
	100	50	25	10		
1170	10^{-7}	10^{-7}	10^{-6}	10^{-6}	10^{-4}	1×10^2
1296	10^{-7}	10^{-7}	10^{-6}	10^{-6}	10^{-4}	1.43
1372	10^{-7}	10^{-7}	10^{-6}	10^{-6}	10^{-4}	1.43
1534	10^{-7}	10^{-7}	10^{-6}	10^{-6}	10^{-4}	0.62×10^2
1578	10^{-7}	10^{-7}	10^{-6}	10^{-6}	10^{-4}	0.7×10^2

Table 2. The analytical enhancement factor (EF) obtained for each Ag film thickness at the limit of detection (LOD) concentration for CV with periodic nanotrenches imprinted, by considering the presence of the main marker bands in the spectral fingerprint.

SERS band (cm^{-1})	Sample thickness (nm)/ SERS LOD (M)				Raman LOD (M)	AEF
	100	50	25	10		
1170	–	–	10^{-12}	10^{-10}	10^{-4}	1.7×10^7
1296	10^{-11}	10^{-10}	10^{-12}	10^{-11}	10^{-4}	2.3×10^7
1372	10^{-11}	10^{-11}	10^{-12}	10^{-11}	10^{-4}	3.3×10^7
1534	–	–	10^{-12}	10^{-11}	10^{-4}	6.5×10^7
1578	–	10^{-10}	10^{-12}	10^{-11}	10^{-4}	1.7×10^7

• An ideal thickness the 25 nm Ag film covering the nanoimprinted trenches in order to provide best SERS performance.

Final remarks

• 3D SERS-active substrates were developed by depositing Ag films onto nanopatterned plastic substrates, fabricated by NIL.
• The contribution of both the Ag film and the nanopatterned structures were determined in the whole AEF obtained. The effect of the Ag nanoclusters induced by DC deposition offer solely an enhancement at best of 10^2.
• When Ag films are deposited on top of the nanopatterned substrate, the synergistic enhancement effect is of 7 orders of magnitude.
• Our findings suggest that the 25 nm silver film covering the nanotrenches imprinted by NIL is the most promising among the 4 different Ag film thicknesses that were tested, with an AEF of 1.7×10^7 and a contribution from the Ag layer of only one order of magnitude.
• Our final purpose is to use these SERS substrates for developing optical biosensors for the detection of bacterial specific signalling molecules.