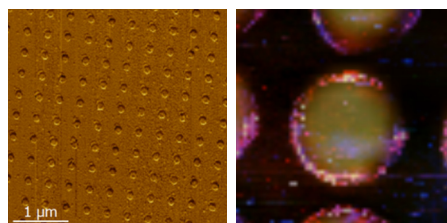


TERS on Functionalized Gold Nanostructures for SERS Application



A. Tempez¹, J-F. Bryche^{2,3}, M. Vega^{2,3,4}, J. Moreau⁴, P.G. Charette^{2,3}, M. Canva^{2,3,4}, T. Brulé¹, T. Carlier¹, M. Chaigneau¹

¹HORIBA FRANCE SAS, Palaiseau, France, ²Laboratoire Nanotechnologies et Nanosystèmes, IRL 3463 – CNRS, Université de Sherbrooke, Sherbrooke, Canada, ³Institut Interdisciplinaire d’Innovations Technologiques 3IT – Université de Sherbrooke - Sherbrooke, Canada. ⁴Laboratoire Charles Fabry, UMR 8501 - CNRS, Université Paris-Saclay, IOGS, Palaiseau, France.

Abstract : This application note reports on TERS characterization of functionalized gold nanodisk arrays on a gold-coated glass substrate that have recently shown impressive results in SERS upon coupled plasmonic modes: the gold layer sustains propagative surface plasmons while the nanostructures sustain localized surface plasmon resonances. Nano-resolved TERS response distribution from grafted thiophenol molecules on nanodisks of 110 and 220 nm diameter feature strong signal localization on the periphery of the nanostructures, in agreement with numerical modeling. We demonstrate how TERS applied on plasmonic nanostructures is an excellent tool to characterize SERS effect distribution at the nanoscale. This work is directly related to the article by JF Bryche *et al.* [1].

Keywords : SERS, plasmonics, biosensors, TERS, Raman spectroscopy, functionalization, gold nanostructures, thiophenol.

Context and issues

Plasmonics is an emerging field making use of the resonant interaction obtained under certain conditions between electromagnetic radiation (light in particular) and free electrons at the interface between a metal and a dielectric material (e.g. air or glass). Surface-enhanced Raman scattering (SERS) is a powerful plasmonics-based analytical technique giving chemical information of molecules or molecular assemblies adsorbed on nanostructured metallic surfaces [2]. For bioanalytical sensor applications, these surfaces are engineered to maximize enhancement factors and molecular specificity.

Potential/ Input from technique

Tip-enhanced Raman spectroscopy (TERS) which provides nanoscale chemical mapping has been used to map the electromagnetic near-field surrounding metal nanostructures [3] and multipolar plasmonic mode inside nanoparticles [4]. As TERS relies on the signal of an ultra confined volume, nano-scale geometry features such as edges or surface heterogeneities and their effect on sensing performance may be probed [5]. Hence TERS mapping of grafted nanostructures aims at confirming model predictions and quantifying SERS sensitivity enhancement. In addition, TERS could help to determine the optimal positioning of target molecules on the sensor surface through spatially selective surface functionalization.

Starting point, what is known?

Gold nanodisk arrays fabricated on continuous gold films deposited glass substrates have recently shown good response in SERS as well in SPR [6] as a result of the presence of coupled plasmonic modes. Indeed, the continuous metal layer sustains propagative surface plasmons while the nanostructures sustain localized surface plasmon resonances. Coupling between them can occur in specific conditions and give rise to hybrid modes with improved characteristics for sensing [7].

Next, an experimental study was conducted to study the effect of thiophenol localization on the SERS response of such gold nanodisks on a continuous gold layer: full coverage (or complete) functionalization was compared with selective_ nanodisks only_functionalization. As illustrated in Fig. 1a, the “selective” sample was prepared upon lifting off a functionalized resist protected substrate (classic nanofabrication). The “complete” sample was prepared upon a second functionalization of the “selective” sample. A reference complete coverage sample was prepared in a one-step functionalization. The $\frac{I_{SERS-Selective}}{I_{SERS-complete\ coverage}}$ ratios of the SERS response (peak intensity of thiophenol 1075 cm^{-1} peak) were measured for three types of nanostructures and at three laser wavelengths (633, 660, and 785 nm) and are shown in Fig. 1b. For all periods and all wavelengths (close and far from plasmonic resonance wavelength) ratios are very close to 1, which means that Raman response comes essentially from the nanostructures.

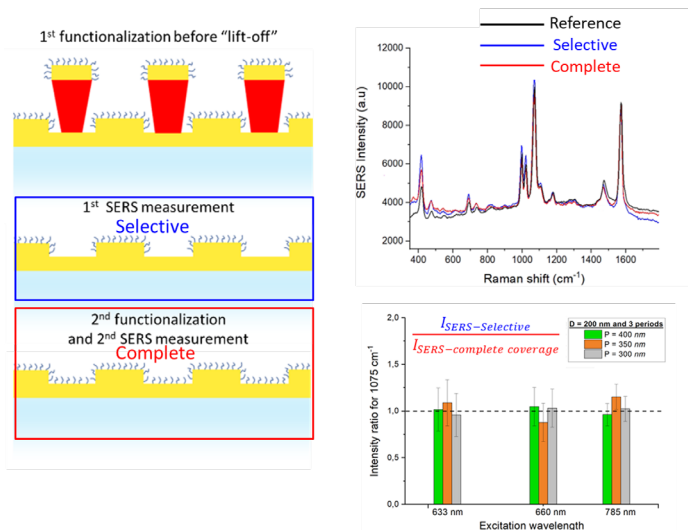


Figure 1 : a) Schematic diagram showing the two-step functionalization of the gold nanostructures based on a lift-off process. b) Superposition of reference, selective and complete surface coverage functionalization SERS spectra (an offset on the y-axis has been applied to show the superposition). c) Ratio of SERS intensity between the selective and complete coverage functionalization at three excitation wavelengths (633, 660, and 785 nm) for the 1075 cm⁻¹ peak.

In parallel, numerical modeling of the electrical field distribution of nanostructured SERS substrates predicts high electrical field at the edges of the nanostructures. This is illustrated by results shown in Fig. 2 for 220 nm diameter disks arranged in a square way of 400 nm period.

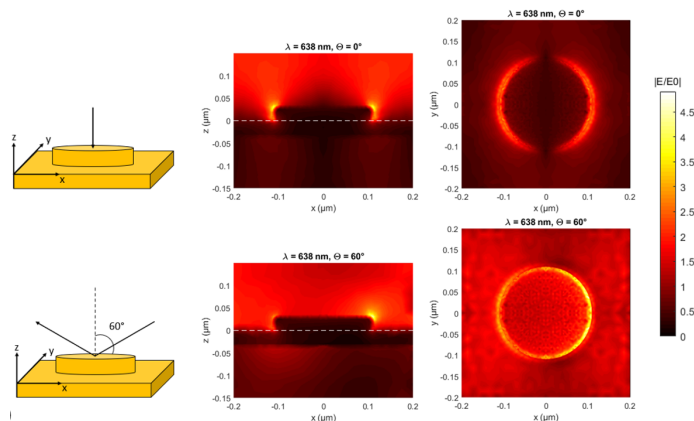


Figure 2 : Side (x, z) and top (x, y) views of the normalized electric field distribution for 220 nm diameter gold nanodisks arranged in a square array of 400 nm period. The disks are excited with TM light at 638 nm with a) 0° incidence and b) 60° incidence angle. The white line outlines the top surface of the 30 nm gold nanofilm.

Here, we present TERS characterization of the same nanostructures that have undergone the selective functionalization. Sub-10 nm resolution TERS mapping will give further insight into localized effects of molecules contributing to the Raman signal. The reader may refer to the article by Bryche *et al* in Nanomaterials [1].

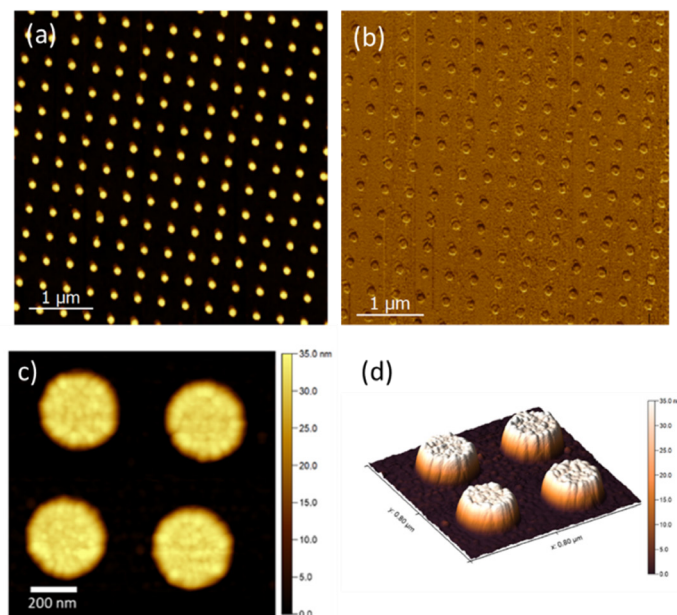


Figure 3 : a) & b) 5x5 μm² height and phase AFM images of an array of uniform gold nanodisks (diameter=100 nm, period=400 nm); c) & d) 800x800 nm² AFM images in 2D and 3D views of the gold nanodisks (diameter=220 nm, period=400 nm) on gold film.

Description of sample and measurement

Measurements were realized on gold nanodisk arrays fabricated on gold films. The nanostructures were prepared by e-beam lithography [3]. The 5x5 μm² scan topography and phase AFM images (Fig. 3.a & Fig. 3.b) confirm a well-defined gold nanodisk array with diameters (D) of 100 nm and a period (P) of 400 nm. 800x800 nm² AFM images (Fig. 3.c & Fig. 3.d) give a height of 32 nm±5 nm for the 220 nm diameter nanostructures.

The samples are functionalized with a 0.1 mM solution of thiophenol (C₆H₆S) over a 2.5 hr incubation time, as required to saturate the gold surface. The samples were then rinsed with ethanol for 5 min and dried with nitrogen. Raman response will be observed for the characteristic Raman peaks of thiophenol at 419/1000 cm⁻¹ (out of plane C-C-C stretching), 1025 cm⁻¹ (out of plane C-H stretching), 1075 cm⁻¹ (C-C-C stretching in-plane and C-S stretching), and 1575 cm⁻¹ (C-C stretching).

TERS measurements were performed with an XploRA Nano system (HORIBA Scientific, France) combining a state-of-the-art scanning probe microscope (OmegaScope) with a Raman micro-spectrometer. The laser excitation (638 nm, 80 μW, p-polarized) is incident on the sample at an angle of 60° to the normal of the sample plane. The laser light is focused using a 100x objective (NA=0.7) mounted on a piezo scanner for precise positioning and focusing of the spot at the apex of the probe tip. The TERS probes were cantilever-based gold or silver coated AFM-TERS tips (OMNI TERS-SNC-Au/Ag, App Nano for HORIBA Scientific).

TERS enhancement was first measured by acquiring Raman spectra with the tip in contact with the sample surface with a typical interaction force of 2–10 nN (labeled “In Contact” in Fig. 4) and with the tip a few nm away from the surface (labeled “No Contact” in Fig. 4), both with acquisition times of 5 s.

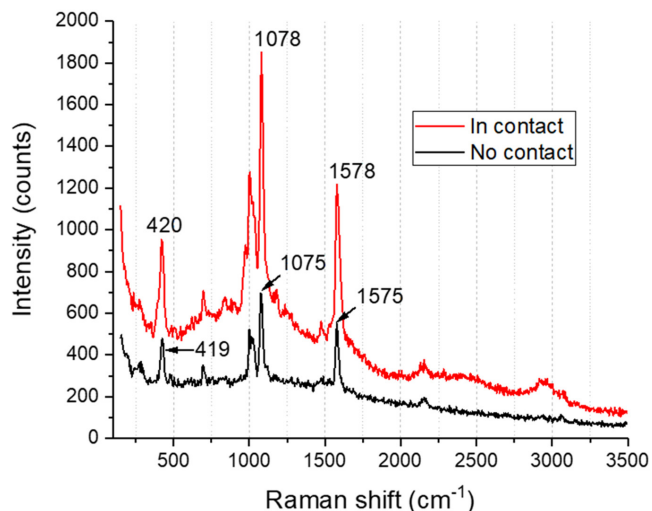


Figure 4: TERS signal confirmation with contact (red curve) and no contact (black curve) measurements at 638 nm with 80 μ W and 5 s of acquisition. The tip is localized on the center of a nanodisk.

Figure 5 shows AFM images (1650 \times 1650 nm²) of the 220 nm gold nanodisks overlaid with corresponding TERS signal amplitude maps from the same area. At each point of the map, we performed TERS spectrum acquisitions with the tip in contact. The samples were displaced laterally in alternating-contact mode between pixels to preserve tip sharpness. High intensities of TERS signals in the zoomed picture correspond to the brightest point and are localized on the edges of the nanodisks, confirming our modeling predictions.

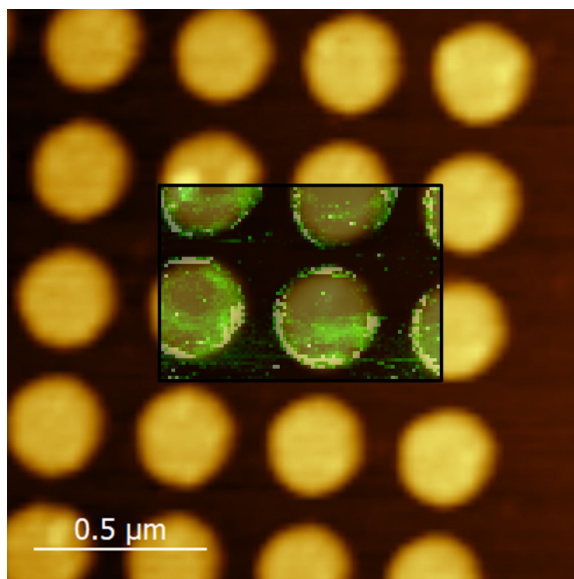


Figure 5: Overlay of TERS intensity (1578 cm^{-1} peak) map over the topographic AFM image, revealing that a higher Raman signal is seen on the edge of the nanostructures. The pixel size in the TERS image is 10 \times 10 nm².

These results agree with a recent lower spatial resolution study [8] realised on gold nanodisks on a Si substrate functionalized with a MoS₂ monolayer.

Fig. 6a results from the same TERS map as Fig. 5 but is shown as an overlay of three characteristic peaks of thiophenol: (Blue) 1078 cm^{-1} peak, (Green) 1578 cm^{-1} peak, and (Red) 2900 cm^{-1} . All three signals are enhanced at the edge of the disks. Fig. 6b displays three Raman spectra averaging 36 spectra from 36 pixels for three regions: inter-disk, disk center, and disk edge.

In addition to higher signal and background, the spectrum of the disk edge region features spectral differences like additional bands at the lower wavenumbers of the 1578 cm^{-1} peak and much higher intensity in the 2900 cm^{-1} band. Surface-enhancement and tip-enhancement effects interleave in the observed spectra. Nevertheless, the spectral differences are linked to the Raman modes surface-enhanced under the 60° illumination as a result of the higher electric field in this direction. Further investigation on the Raman bands will be realized to compare with theoretical orientation of the molecule on the surface and check if the enhanced modes correspond to the molecular orientation. The TERS configuration with a 60° angle illumination in flat sample enhances modes perpendicular to the surface. Thus this TERS geometry act as a nanoprobe for SERS and allows to nanolocalize SERS hot spots based on spectral modes.

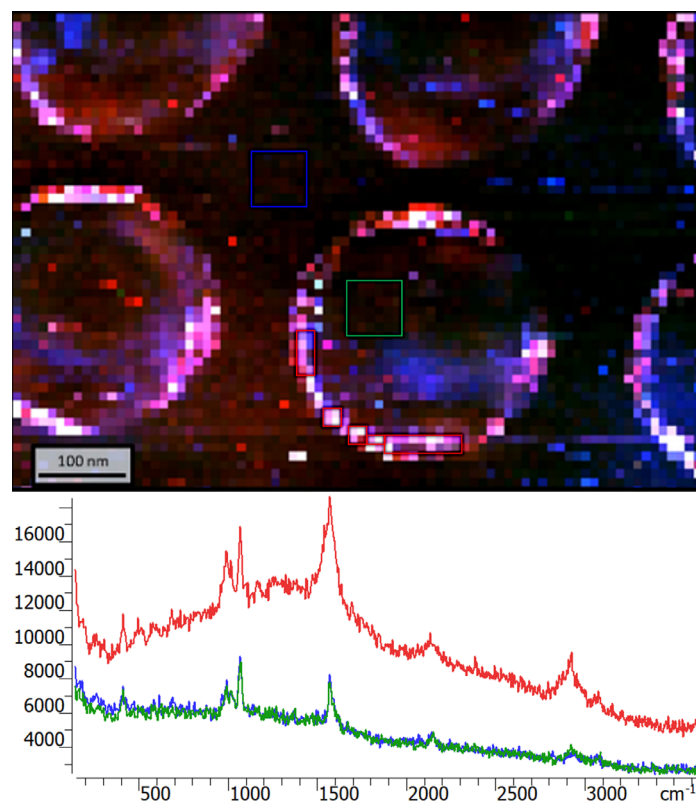


Figure 6: a) Overlay of three TERS intensity maps of 220 nm gold nanodisks with a 638 nm laser: (Blue) 1078 cm^{-1} peak, (Green) 1578 cm^{-1} peak, and (Red) 2900 cm^{-1} peak. b) TERS average spectra (36 pixels area) from three identified regions of the sample: disk center, disk edge and inter-disks.

Conclusion and perspectives

This application note shows how TERS mapping is capable of characterizing SERS nanostructures. Through high-resolution TERS measurements (sub-10 nm), we have shown that molecules grafted onto the edge of the nanostructures edges exhibit higher TERS intensity, which is in line with modeled electric field distribution and preliminary SERS response measurements on complete and selective molecular coverage samples.

In addition, the spectral differences observed between the in and out areas of the SERS hot spots confirm that despite interleaved surface-enhanced and tip-enhanced effects, TERS with a side illumination/collections configuration applied on plasmonic nanostructures is an excellent tool to characterize SERS effect distribution at the nanoscale.

These measurements suggest that deliberate and accurate positioning of target molecules at locations of high field concentrations on the nanostructures is advantageous for optimizing detection sensitivity and speed, especially at low molecular concentrations.

Acknowledgments

M. Vega is supported by an international doctoral scholarship from IDEX Paris-Saclay (ANR-11-IDEX-0003-02).

References

1. J.-F. Bryche, M. Vega, A. Tempez, T. Brulé, T. Carlier, J. Moreau, M. Chaigneau, P.G. Charette, M. Canva, *Nanomaterials*, vol 12, no. 20, pp. 3586-3697, Oct. 2022. <https://www.mdpi.com/2079-4991/12/20/3586>
2. E. Le Ru, *Principles of Surface-Enhanced Raman Spectroscopy*. Elsevier, 2009.
3. A. Bhattarai, K. T. Crampton, A. G. Joly, L. Kovarik, W. P. Hess, and P. Z. El-Khoury, *J. Phys. Chem. Lett.*, vol. 9, no. 24, pp. 7105–7109, Dec. 2018.
4. A. Bhattarai, B. T. O’Callahan, C.-F. Wang, S. Wang, and P. Z. El-Khoury, *J. Phys. Chem. Lett.*, vol. 11, no. 8, pp. 2870–2874, Mar. 2020.
5. P. Z. El-Khoury and Z. D. Schultz, “From SERS to TERS and Beyond: Molecules as Probes of Nanoscopic Optical Fields,” *J. Phys. Chem. C*, vol. 124, no. 50, pp. 27267–27275, Oct. 2020.
6. J.-F. Bryche, F. Hamouda, M. Besbes, P. Gogol, J. Moreau, M. Lamy de la Chapelle, M. Canva, and B. Bartenlian, *Micro and Nano Engineering*, vol. 2, pp. 122–130, Mar. 2019.
7. M. Sarkar, M. Besbes, J. Moreau, J.-F. Bryche, A. Olivéro, G. Barbillon, A.-L. Coutrot, B. Bartenlian, and M. Canva, *ACS Photonics*, vol. 2, no. 2, pp. 237–245, Jan. 2015.
8. M. Rahaman, A. G. Milekhin, A. Mukherjee, E. E. Rodyakina, A. V. Latyshev, V. M. Dzhagan, and D. R. T. Zahn, *Faraday Discuss.*, vol.214, pp. 309–323, 2019.



Picture of the XploRA Nano system combining the OmegaScope scanning probe microscope with the XploRA Raman micro-spectrometer

info.sci@horiba.com

USA: +1 732 494 8660
UK: +44 (0)1604 542 500
China: +86 (0)21 6289 6060
Taiwan: +886 3 5600606

France: +33 (0)1 69 74 72 00
Italy: +39 06 51 59 22 1
India: +91 (80) 4127 3637
Brazil: +55 (0)11 2923 5400

www.horiba.com/scientific

Germany: +49 (0) 6251 8475 0
Japan: +81(75)313-8121
Singapore: +65 (6) 745-8300
Other: +33 (0)1 69 74 72 00

HORIBA
Scientific