

**SURFACE ENHANCED RAMAN SCATTERING OPTIMIZATION
OF GOLD NANOCYLINDER ARRAYS : INFLUENCE OF THE
LOCALIZED SURFACE PLASMON RESONANCE
AND EXCITATION WAVELENGTH**

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ABSTRACT. We here emphasize that the Surface Enhanced Raman Scattering (SERS) intensity has to be optimized by choosing the appropriate gold nanoparticles size for two excitation wavelengths: 632.8 and 785 nm. We discuss the role of the position and of the order of the Localized Surface Plasmon Resonance (LSPR) in such optimization for both wavelengths. At 632.8 nm, the best SERS intensity is reached for a LSPR located between the excitation and Raman wavelengths whereas at 785 nm, the LSPR should be placed outside this range. The third order of LSPR is shown to have no influence on the SERS intensity.

1. Context and aim of this work

The size-dependant optical properties of noble metal nanoparticles have been intensively studied in the last twenty years and exploited in many applications and notably for bio- or chemical sensors. The main parameter of these properties is the Localized Surface Plasmon Resonance (LSPR) known to generate a strong local enhancement of the electromagnetic field at the vicinity of metallic nanoparticles. This phenomenon is the basis of the Surface Enhanced Raman Scattering (SERS). The Raman intensity, intrinsically weak, of a molecule adsorbed at a metallic nanoparticles surface benefits from this strong local field enhancement to provide the so called electromagnetic effect. The final SERS intensity can then be expressed as following: $I_{SERS} = f^2(\lambda_0) \cdot f^2(\lambda_R) \cdot |E|^2$ where $f(\lambda_0)$ and $f(\lambda_R)$ are respectively the enhancement factors at the excitation and Raman wavelengths and E is the electromagnetic field. SERS effect can be obtained with various kinds of metallic nanostructures. For example, we have worked on SERS effect obtained by deposition of gold colloidal solution.

But this chemical way of SERS substrate synthesis presents two major drawbacks; firstly, nanoparticle structures and SERS response are not reproducible and secondly, the associated LSPR is not easily tuned to the excitation wavelength. On the opposite, nanolithographic techniques are known to provide a very good control of the size and the shape

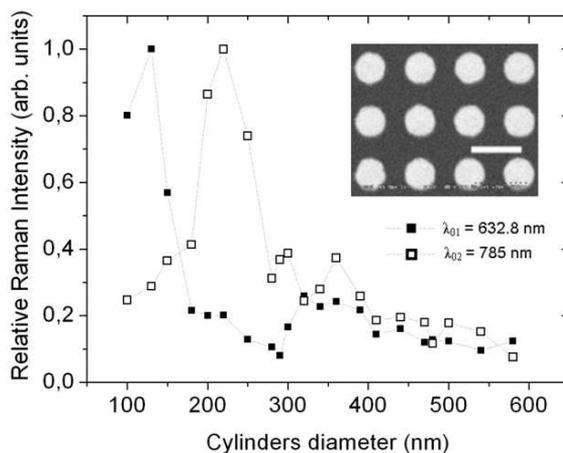


Figure 1. Evolution of the relative Raman Intensity (acquisition time: 10 s) versus the nanocylinder diameters for two excitation wavelengths $\lambda_{01} = 632.8$ nm (black squares) and $\lambda_{02} = 785$ nm (white squares). For each curve, the SERS intensity has been normalized. The dotted lines are just used here as indicators of the trends. Inset: SEM image of a SERS-active substrate composed of gold nanocylinder array (diameter = 270 nm, height = 50 nm, scale bar = 500 nm).

of the nanoparticles deposited on the substrate. This allows a precise control of the LSPR and, thus, of the Raman enhancement.

In the case of nanocylinder or nanotriangle arrays, the best Raman enhancement is reached for a LSPR position between the excitation and the Raman wavelengths whereas it is not always the case for other shapes like nanowires. Moreover, in this latter case, it has been demonstrated the strong influence of the higher order of LSPR on SERS. Thus, by using a large range of cylinder diameters, we have studied the SERS efficiency of nanocylinder arrays at two excitation wavelengths: 632.8 and 785 nm, to determine the influence of the position and of the order of the LSPR on the SERS intensity.

2. Materials and methods

The gold nanocylinder arrays are fabricated on glass substrates by electron beam lithography and lift-off techniques. The nanocylinder diameter varies from 80 to 580 nm whereas their height is kept constant at 50 nm. A layer of Cr of 3 nm is also used to improve adhesion of gold on glass. The gap between two nanocylinders is also kept constant around 200 nm. Thus, the distance between particles is large enough to avoid any near field coupling and, therefore, no effect on the LSPR position or the SERS signal. The nanocylinder shape, size, and array parameters were checked by scanning electron microscope. For SERS measurements, the substrates were immersed in a 10^{-3} M solution of a probe molecule, the trans-1,2-bis-4-pyridyl-ethylene (BPE), during 1 h and dried. Extinction and Raman spectra were recorded with a Labram Jobin–Yvon micro-Raman spectrophotometer.

3. Conclusions

In this work [1], we demonstrated the optimization abilities of the SERS intensity provided by arrays of gold nanocylinders. In fact, for nanocylinders with 130 nm diameters, we obtain the best SERS intensity with a corresponding LSPR position between the excitation 632.8 nm and Raman wavelength (Figure 1). However, with an excitation wavelength of 785 nm, the best SERS intensity is obtained for a corresponding LSPR outside the area excitation-Raman wavelengths. We can assume that the link between the LSPR measured in far field extinction spectroscopy and the SERS signal considered as a near field process is not straightforward. Indeed, as it has yet been demonstrated by Grimault *et al.* [2] the field enhancement in the near field and at the vicinity of the nanoparticles surface is not directly related to the plasmon intensity. There is actually some shift between the plasmon resonance maximum and the maximum field enhancement reached at the particle surface. Thus, it is of real importance to consider this fact for the SERS optimization, especially in the case of SERS sensor development. Finally, the higher orders of the LSPR resonances have been shown to have a very low influence on the SERS intensity.

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