Surface enhanced Raman scattering optimization of gold nanocylinder arrays: Influence of the localized surface plasmon resonance and excitation wavelength

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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. © 2010 American Institute of Physics. [doi:10.1063/1.3462068]

The size-dependant optical properties of noble metal nanoparticles have been intensively studied in the past 20 years and exploited in many applications and notably for bioor chemical sensors.¹ 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.² This phenomenon is the basis of the surface enhanced Raman scattering (SERS).^{2,3} 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: $I_{\text{SERS}} = f^2(\lambda_0) \times f^2(\lambda_R) \times |E|^2$ where $f(\lambda_0)$ and $f(\lambda_R)$ are, respectively, the enhancement factors at the excitation and Raman wavelengths^{4–6} 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.⁷ But this chemical way of SERS substrate synthesis presents two major drawbacks; first, nanoparticle structures and SERS response are not reproducible and second, 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 of the nanoparticles deposited on the substrate. This allows a precise control of the LSPR⁸ and, thus, of the Raman enhancement.^{4,5,9–12}

According to Refs. 5, 10, and 12 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.⁹ Moreover, in this latter case, it has been demonstrated the strong influence of the higher order of LSPR on SERS.^{9,13} Thus, by using a large range of cylinder diameters, we have studied the SERS efficiency of nanocylinder arrays at following 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.

The gold nanocylinder arrays are fabricated on glass substrates by electron beam lithography and lift-off techniques (for more details, see Ref. 12). 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 (SEM) (Fig. 1).

For SERS measurements, the substrates were immersed in a 10^{-3} M solution of a probe molecule, the *trans*-1,2bis(4-pyridyl)ethylene (BPE), during 1 h and dried. Extinction and Raman spectra were recorded with a Labram Jobin– Yvon micro-Raman spectrophotometer (for technical details, see Ref. 14).

As shown in Fig. 1, when the diameter of the nanocylinders increases, the Raman signal reaches clearly a maximum for a diameter of 130 nm for an excitation wavelength of 632.8 nm and is very high compared to the majority of the other diameters (around one order of magnitude). In addition, no other maximum can be clearly observed on this curve. This result, obtained on a large range of diameters, confirms that this kind of SERS-active substrate must be optimized by choosing the appropriate size.^{9,12}

The role of the LSPR generated by the nanolithographied substrate has been clearly identified. Indeed, as it is well known, the position of the LSPR is redshifted for higher diameter and higher mode of resonance (third order in our case) is also observed for large nanocylinders (diameter higher than 300 nm). In fact, for arrays of gold nanocylin-

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FIG. 1. Evolution of the relative Raman intensity (acquisition time: 10 s) vs the nanocylinder diameters for two excitation wavelengths λ_{01} =632.8 nm (black squares) and λ_{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 gold nanocylinder array (diameter =270 nm, height=50 nm, and scale bar=500 nm).

ders, some have shown that the best Raman signal enhancement is obtained (Fig. 2) for the LSPR position λ_{LSPR} located exactly between the excitation wavelength λ_0 and the Raman wavelength λ_R (related to the band of interest of the probe molecule observed).^{5,12} More precisely, some have proposed that it should correspond to $\lambda_{LSPR} = (\lambda_L + \lambda_R)/2$.⁵ Then, for excitation at λ_{01} =632.8 nm and a Raman wavelength λ_{R1} at 685 nm (BPE band at 1200 cm⁻¹), the best LSPR position should be located at 659 nm. For the first and third order, the corresponding nanocylinder diameters are, respectively, close to 130 nm and to 400 nm (Fig. 2). As shown in Fig. 3, this "rule" is effectively verified for the dipolar like LSPR mode whereas we can notice that the third order of resonance has few SERS activities. Indeed, looking at the Fig. 1, it is clear that there is no significant magnification of the Raman



FIG. 2. Evolution of the LSPR position vs the cylinder diameter for the first order (black squares) and the third one (white triangles). λ_{01} and λ_{02} correspond, respectively, to the excitation wavelengths at 632.8 and 785 nm. λ_{R1} and λ_{R2} are, respectively, the Raman wavelengths of the BPE band at 1200 cm $^{-1}$ when excited at λ_{01} and λ_{02} . The dotted lines show the average position between λ_0 and λ_R for both excitation wavelengths.



FIG. 3. Relative Raman Intensity vs the LSPR positions for the two excitation wavelengths λ_{01} =632.8 nm (a) and λ_{02} =785 nm (b) and reminder of the positions of the excitation and Raman wavelengths for each cases.

signal for diameters around 400 nm. It means that for this shape, the higher orders of resonance have few effects on the Raman signal. This behavior is opposite from the one observed with elongated nanoparticles like nanowires where the higher orders have strong SERS activity which can even be higher than the dipolar mode.⁹

We have also investigated the SERS efficiency of the nanocylinders with another excitation wavelength λ_{02} =785 nm. Now, if we apply the rule previously observed for 632.8 nm, the best Raman enhancement should be obtained for a λ_{LSPR} close to 820 nm since the Raman wavelength λ_{R2} is located at 859 nm. For the first order, the corresponding cylinder diameter is close to 300 nm. Referring to the Fig. 1, we clearly see a strong peak a SERS intensity maximum for a diameter of 220 nm and not 300 nm as expected. Thus, as shown on Fig. 3(b), the best Raman signal is obtained for a λ_{LSPR} close to 750 nm largely outside the $\lambda_{02} - \lambda_{R2}$ range and the optimal LSPR is strongly shifted compared the expected wavelength. This observation gives evidence that the "rule" indicating that the λ_{LSPR} should be located in the $\lambda_0 {-} \lambda_R$ range is not applicable on the whole visible range and strongly depends on the excitation wavelength used. 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

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yet been demonstrated by Grimault *et al.*,¹⁵ the field enhancement in the near field and at the vicinity of the nanoparticle surface is not directly related to the plasmon intensity. There is actually some shift between the plasmon resonance maximum and the maximum field enhancement reaches 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.

In this work, 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. However, with an excitation wavelength of 785 nm, the best SERS intensity is obtained for a corresponding LSPR outside the area excitation-Raman wavelengths. 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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