SPECTRAL DEPENDENCE OF THE AMPLIFICATION FACTOR IN SURFACE ENHANCED RAMAN SCATTERING

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ABSTRACT. Multi-wavelength SERS measurements on dyes molecules adsorbed on gold evaporated nanoparticles substrates are presented. The spectra are correlated with the Localized Surface Plasmon Resonance (LSPR) profile of the nanostructured substrate before and after the adsorption process. The enhancement of the typical vibrational modes of the methylene blue is investigated for the different excitation wavelengths and we show that its behavior follows properly the LSPR profile of nanoparticles "dressed" with the dye molecules.

1. Introduction

Surface enhanced Raman scattering (SERS) allows the detection of molecules adsorbed on noble metal nanoparticles (Ag, Au, Cu, etc.) at sub-micro molar concentrations. A strong signal amplification (up to 10^{8-10}) is obtained when both the excitation and the Raman photons frequencies (ω_L and ω_R, respectively) match the localized plasmon resonances (LSPR) of the nanoparticles (NP). The spectral dependence of both the excitation field enhancement factor $A_{exc}(\omega)$ and of the re-radiation enhancement factor $A_{rad}(\omega)$ have been observed to be proportional to the LSPR profile, $Q(\omega)$ [1, 2]. The spectral dependence of $Q(\omega)$ is therefore particularly important since it determines both the best excitation wavelength for optimal SERS detection and the re-radiation enhancement of the Raman modes. It is still not known, however, whether the effective $Q(\omega)$ refers to the LSPR of the bare NPs or to the resonance of the NPs "dressed" with the probe molecules [$Q_{dress}(\omega)$]. The latter is typically energy shifted and can be much broader, according to the molecular dielectric constant. To get insight on this phenomenon we carried out multi-wavelength (515nm, 633nm, 785nm) SERS experiments using evaporated gold nanoparticles as SERS-active substrates on which we deposited Methylene Blue molecules which notably alter the LSPR profile [3]. The SERS peaks intensities are normalized to the Raman intensities measured on powder samples. The results are compared with experiments carried out on Mercaptopyridine and L-Tyrosine molecules, which do not affect the LSPR profile.
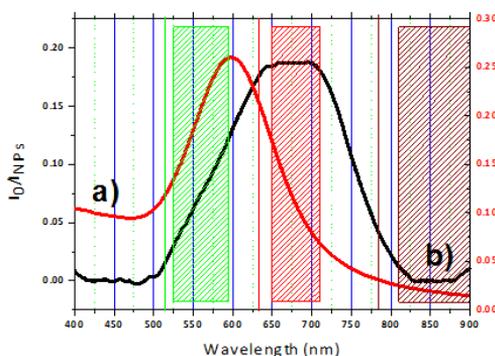
Figure 1. Extinction spectra of (a) bare gold NPs and (b) after the binding of Methylene Blue molecules. The three colored lines indicate the SERS excitation laser wavelengths.

2. Experimental

The gold clusters were prepared by Electron Beam Evaporation (EBE) on SiO_2. The sample was heated at $480°C$ and a gold amount of $1 \times 10^{16} cm^{-2}$ was evaporated. Gold atoms arrive in the heated substrate, so they have the possibility to diffuse over the substrate, immediately starting a ripening process leading to cluster formation. The dye solutions were prepared mixing deionized water with the powder of Methylene Blue (Carlo Erba Reagenti), L-Tyrosine (Sigma-Aldrich) and 4-Mercaptopyridine (95% - Sigma-Aldrich) at the concentration of 10^{-4} M, 10^{-2} M and 10^{-2} M, respectively. The samples of gold NPs were, then, soaked into aqueous solution of dye for 1 h and then dried in vertical position to avoid formation of too thick multilayer of molecules on substrates. SERS experiments were carried out with a HR800 – Jobin Yvon micro-spectrometer coupled with an Ar++ (515 nm), a HeNe (633 nm) and a diode (785 nm) laser for multi-wavelength excitation. Measurements were done focusing a few tens of W of laser power on a submicron spot using a 100X microscope objective (NA 0.95). All the spectra were acquired with integration time from 10 to 60 seconds.

3. Results and discussion

Figure 1 shows the different LSPR profiles between the bare NPs (red line) and "dressed" NPs (black line). The presence of a layer of Methylene Blue molecules bound to the gold NPs substrate yields a resonance energy red-shift of about 27 nm (from 596 nm to 633 nm) and a broadening of 50 nm. With the three excitation wavelengths of our apparatus, we were able to excite the ascending, central and descending region of the dressed LSPR profile $Q_{dress}(\omega)$ (colored lines in Fig. 1). The Raman spectrum of MB extends in the 400 – 1650 cm^{-1} region with most intense peaks at 450 cm^{-1} and 1620 cm^{-1} (Fig. 2, black lines). The SERS spectra at the investigated excitation wavelengths (fig. 2, colored lines) display a different intensity ratio of the 450 cm^{-1} and 1620 cm^{-1} peaks with respect to the
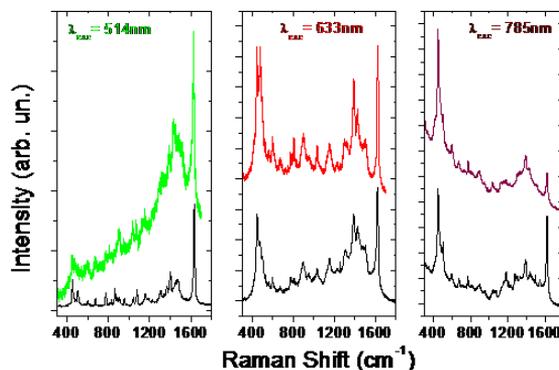
Figure 2. Comparison between Raman Spectra of Methylene Blue in powder (black lines) and SERS spectra (colored lines) at different excitation wavelengths.

Raman counterpart. While at 515nm (green line) the 1620 cm^{-1} mode is more enhanced with respect to the peak at 450 cm^{-1}, at 785 nm (wine line) the opposite is observed. At 633 nm (red line) the two modes experience the same enhancement factor. This behavior is compatible with the hypothesis that $A_{rad}(\omega) \propto Q_{dress}(\omega)$ since $Q_{dress}(\omega)$ is almost flat around 633 nm and extends beyond 785nm. In the case of $A_{rad}(\omega) \propto Q_{bare}(\omega)$, instead, we should expect no SERS at 785 nm (excitation is completely out of the LSPR profile) and a preferential enhancement of the 450 cm^{-1} mode with respect to the 1620 cm^{-1} one at 633 (we are in the descending part of the LSPR profile, fig. 1 blue line), which is not the case.

4. Conclusions

In conclusion we show that for MB molecules on nanostructured gold substrates the normalized relative SERS intensities follow remarkably well the $Q_{dress}(\omega)$ surface plasmon resonance profile and that this is the spectrum that defines the re-radiation enhancement factor of the SERS modes.

Acknowledgments

References

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