Surface Enhanced Raman Spectroscopy of different chain length PEP+ moiety bound to Nanorods

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In recent years, Surface Enhanced Raman Spectroscopy (SERS) has become one of the most important technique for characterizing the chemical structure and monitoring structural changes at the single-molecule level.[1] The key effect for the observation of enhanced Raman signals is the favorable optical properties of metal nanostructures, based on their local surface plasmon. The enhancement depends on the type of metal and nanostructures. Several examples of nanostructures of different shape, metal and, eventually, regularly assembled are reported in the literature, resulting in SERS enhancement factors up to 10^8.[2-6] For example, rod-shaped nanoparticles present a highly tunable longitudinal plasmon band which should be exploited to amplify both the exciting laser and the scattered field in SERS measurements. Despite the desirable characteristics of metallic nanorods, as SERS substrates, only few reports exist for SERS on nanorods where the Raman excitation occurs at a wavelength that overlaps with nanorod plasmon resonances.[7-12]

In this presentation, we report our recent results on the amplification of the Raman signals of 1-(*N*-methylpyrid-4-yl)-2-(*N*-methylpyrrol-2-yl)ethylene (**PEP+**)) using gold nanorods (NRs) as substrate. The dipolar positively charged dye **PEP+** is a push-pull molecule composed by a π-deficient (pyridinium ion) as acceptor group A and a π-excessive (pyrrole) heterocycle as donor group D.[13] **PEP+** or its derivatives present resonant and non-resonant nonlinear optical properties, such as two-photon absorption or second harmonic generation.[14-15] We have synthesized thiol-acetyl terminated **PEP+** chromophores spaced by two linear alkyl chains of different length, containing 3 or 12 carbon atoms.

The basic idea is to control the intensity of the Raman signals as a function of the distance between the dye and the metallic surface of the metal nanostructure and to study both the effect of the laser resonance with the absorption band of **PEP+** moiety and with the two plasmon modes.

Raman characterization of NRs, functionalized with **PEP+C3SH** and **PEP+C12SH,** both deposited on glass substrates and in solution, is realized using different laser excitation lines. The 488-nm and the 514-nm laser excitation lines are in resonance with the absorption band of the molecules, performing Surface Enhanced Resonance Raman Scattering (SERRS), whereas the 785-nm laser excitation line is out of resonance. Moreover, the 514-nm and the 785-nm lines are resonant with the transverse and longitudinal modes of gold nanorods, respectively, suggesting a further enhancement of the Raman signals.

Comparing Raman spectra, for the same dye bound to NRs, at different laser excitation lines, turns out that data measured by exciting at 514 and 785-nm present a higher signal-to-noise ratio than that at 488 nm. This consideration suggests that the amplification is higher when the laser excitation wavelength is resonant with the two plasmon modes than, exclusively, with the absorption band of the dye, as for the 488-nm radiation.[10] Anyway, the resonance condition of the 514-nm laser excitation with the absorption band of the dye strongly contributes to the amplification of the Raman signal. In fact, DDA calculations, performed on our nanorods, reveal that the local field is about 10 times higher when the longitudinal plasmon mode is excited instead of the transverse one. This means that, in resonance with the longitudinal and transverse plasmon modes, we predict an enhancement of the Raman signal of about 10^4 and 10^2, respectively, which is not confirmed by the measurements if we don't take into account the resonance with the absorption band of the dye.

To compare the amplification of Raman response when the transverse and longitudinal plasmon modes are excited, we evaluated the enhancement factor (EF) using 4-mercaptopyridine (**4-MPy**) as a standard analyte.[10] **4-MPy**, unlike **PEP+** moiety, is not fluorescent and allows us to perform experiments using both 514 nm and 785 nm laser excitation. At 514-nm laser excitation, no signal is observed for **4-MPy** bound to NRs due to the rather low EF. This result clearly agrees with the DDA model prediction for the local field when the transverse mode is excited and further supports our hypothesis of a strong contribution to the SERRS response from the resonance with the absorption band of **PEP+** moiety.

On the other hand, some Raman bands of **4-MPy** bound to NRs are strongly amplified when excited with 785-nm laser excitation. Characteristic ring breathing modes are observable at 1004 cm^{-1} (ν(C–C) mode) and at 1119 cm^{-1} (ν(C–S) mode). The latter is remarkably shifted in **4-MPy** bound to NRs (1094 cm^{-1}) and experiences a dramatic increase in intensity compared with the corresponding Raman signal in solution. The evaluated EF for the ν(C–C) ring breathing mode at 1004 cm^{-1} and the ν(C–S) ring breathing mode at 1119 cm^{-1} are 4.0×10^4 and 1.2×10^5, respectively, perfectly comparable with the DDA calculation.

These preliminary results show as it is important to control the resonance condition with both the plasmon mode and with the electronic transitions of the molecules. In this way, it is possible to obtain a higher amplification and to detect lower levels of chemical species required for sensoristic applications.

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