# Examination of different silver nanostructures for near infrared excited surface-enhanced Raman and hyper-Raman scattering

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Hyper-Raman scattering, the two-photon analogue of normal Raman scattering, follows different selection rules compared to other vibrational spectroscopic methods and can thus give additional spectral information. The very confined excitation volume for this nonlinear process can provide morphological information with high spatial resolution. Together with the near infrared wavelengths that are used for the excitation of hyper-Raman scattering, this is especially useful for the examination of biological cells and tissues. As the intensity of hyper-Raman scattering is very low, it is advantageous to utilize surface enhancement from metal nanostructures to observe hyper-Raman spectra at low molecular concentrations. Finding appropriate nanostructures for surface-enhanced hyper-Raman scattering (SEHRS) can present as more critical than for one-photon Raman scattering, because of the large gap between the excitation wavelength in the near infrared and the scattering wavelength in the visible.
We examined different kinds of silver nanostructures by combining 1064-nm excited SEHRS with one-photon surface-enhanced Raman scattering at 1064 and 532 nm respectively, all in one microspectroscopic setup. The silver nanostructures are able to generate large enhancement in both wavelength regions, although their plasmon resonance frequency is far away from the near infrared excitation wavelength. As a model system we used *para*-mercaptobenzoic acid, whose Raman spectrum changes with the pH value of the surrounding solution [1] and which has been used for pH-sensing before [2]. Depending on the excitation regime, the sensitive differentiation of local pH values is possible in different pH ranges. Furthermore, the evaluation of the surface-enhancement at the two different excitation wavelengths compared to the enhancement of hyper-Raman scattering allows for conclusions about both the plasmonic properties of the nanostructures and the interaction between molecules and the metal surface.

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