

Wavelength-specific Response of Surface-enhanced Raman Scattering in Nanoparticle Dimer Structures

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Raman scattering, the inelastic scattering of light by molecular bonds, provides highly relevant, intrinsic chemical information about samples with a spatial resolution near the diffraction limit, and is thus of highest interest in biomedical applications [1]. It is, however, limited by a fairly low sensitivity, e.g. when compared to fluorescence excitation, due to the low scattering cross section of most organic molecules. A number of techniques have been developed to overcome this limitation, one of which is surface-enhanced Raman scattering, which makes use of the local field enhancement that occurs near plasmon-resonant nanoparticles [2]. Coherent oscillations of the electrons or plasmons in noble metal nanoparticles are known to exhibit coupling effect, when nanoparticles are in close proximity. When organic molecules are used to specifically link nanoparticles and cause the formation of nanoparticle dimers, very small gap dimensions can be reached, resulting in significant near-field enhancement of the electric field in the gap between the particles [3,4]. We studied the wavelength-dependent response of a rodlike acetyl-protected dithiol polymer molecule bridging two gold nanoparticles with a diameter of 40 nm. The introduction of the dithiol polymer leads to the formation of nanoparticle complexes, such as monomers, dimers, and higher order aggregates in suspension, and also serves as a probe for the local field enhancement. We investigated the change in the SERS enhancement factor as a function of the excitation wavelength in the VIS- and NIR-range. With these constructs, it is also possible to estimate the influence of the electromagnetic and chemical enhancement factors depending on the excitation wavelength by comparing peak ratios of different chemical groups within the gap between dimerized nanoparticles.

References:

- [1] Wachsmann-Hogiu, S., T. Weeks, and T. Huser, Chemical analysis *in vivo* and *in vitro* by Raman spectroscopy-from single cells to humans. *Current Opinion in Biotechnology* **20**(1),63-73 (2009).
- [2] Stiles, P.L., J.A. Dieringer, N.C. Shah, and R.R. Van Duyne, Surface-Enhanced Raman Spectroscopy. *Annual Review of Analytical Chemistry* **1**, 601-626 (2008).
- [3] Michaels, A.M., J. Jiang, and L. Brus, Ag nanocrystal junctions as the site for surface-enhanced Raman scattering of single Rhodamine 6G molecules. *Journal of Physical Chemistry B*. **104**(50),11965-11971(2000).
- [4] Laurence, T.A., G. Braun, C. Talley, A. Schwartzberg, M. Moskovits, N. Reich, and T. Huser, Rapid, Solution-Based Characterization of Optimized SERS Nanoparticle Substrates. *Journal of the American Chemical Society* **131**(1), 162-169 (2009).