

Single base resolution by Tip-enhanced Raman scattering

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Recent experiments demonstrate an extremely high lateral resolution of tip-enhanced Raman scattering (TERS) that can be utilized to investigate single bases in a single strand. Interestingly such a high spatial resolution is unexpected when the basic dimensions of the plasmonic probe are considered. The probe consists in our case of an evaporated silver island film on a commercially available AFM probe. The diameter of the more-or-less spherical particles at the tip apex is about 20-30 nm. Considering such size parameters an enhancement area of approximately 5 nm could be expected, generally much too large for a single base detection. A closer look at the actual plasmonic nanoparticles reveals however, that a smooth round surface is not observed, but rather crystalline surfaces that lead to planes, edges, and corners. Under such conditions in fact a single atom must be the front most feature that “touches” the sample. Here we will investigate the effect of a single atomic scale plasmonic feature on the field confinement of a spherical nanoparticle. For this purpose the entire system will be numerically modeled utilizing commercially available finite element methods (Comsol).

In addition we also discuss the effect of a single atom or metal cluster on the polarisability of an investigated molecule. This so-called chemical effect also contributes to the overall enhancement factor in normal surface-enhanced Raman scattering (SERS) and in the specific case of TERS the localization can be precisely controlled and even “unfavorable” positions can be addressed. Here quantum chemical calculations on the DFT level indicate spectral variations and enhancement changes even on a sub-molecular level.[1]

Last not least TERS data on single DNA strand will be shown to compare the above hypotheses with actual experiments.[2]

[1] Latorre, F. et al. *Nanoscale* 8, (2016) 10229–10239.

[2] Lin, X.-M. et al. *arXiv:1604.06598v1* (2016).