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### Lithographic metal nanostructures for tip-enhanced spectroscopic methods

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#### Summary

The plasmonic properties of metallic nanodiscs and nanocones have been characterized with a view to applying them to high performance tip enhanced spectroscopic methods. The characterization used a setup based on the coupling of an achromatic inverted microscope equipped with a total internal reflection objective and an atomic force microscopy (AFM). Tunable plasmonic resonances are identified and are in excellent agreement with numerical simulations. The simulated and measured plasmonic response of the nanostructures suggest possible applications in a new generation of probes for tip-enhanced optical spectroscopy in which plasmonic nanostructures are designed at the apex of a non-metallic AFM tip. The tips enable a spectral tunability as a function of the specific material, the size, shape and topography, together with high electric field enhancement factors. The result in term of tip performances are better than those commonly used in tip-enhanced optical spectroscopy experiments such as tip-enhanced Raman spectroscopy (TERS)<sup>1</sup>.

#### 1. Introduction

Accessing the optical spectroscopic properties of molecules and nanostructures with a spatial resolution less than the diffraction limit of light requires an electromagnetic field that is confined at the nanoscale. This can be achieved by designing and fabricating high performance optical scanning tip probes using micro and nanotechnologies. This approach leads to advanced techniques such as tip-enhanced Raman spectroscopy (TERS), which can be used for concurrent chemical and physical surface mapping with a nanoscale spatial resolution<sup>2</sup>. Such scanning probes benefit from the support of propagative and/or localized surface plasmons whose excitation results in an enhanced and spatially-confined optical evanescent field at the tip. The dimensions of the latter govern the spatial resolution of the technique. In the case of TERS, the amplification factor (typically in the range of  $10^4$  to  $10^8$ )<sup>3</sup> depends strongly on the shape of the tip-enabling TERS mapping with a nanometer resolution. Here we investigate the plasmonic properties of individual nanofabricated gold nanodiscs and nanocones with numerical simulation and darkfield spectroscopy in order to assess their potential for high-performance tip-based optical spectroscopies.

#### 2. Methods and discussion

The plasmonic nanostructures consist of either gold nanodiscs or gold nanocones lithographically patterned onto a glass substrate. The structures have been fabricated by evaporation through resist *lift-off* mask obtained using electron beam (ebeam) lithography<sup>4-5</sup>. The nanostructures are characterized using an in-house optical darkfield set-up in transmission mode, recording the scattering spectrum in the 400-900 nm wavelength range. To enable a comparison with experiments, theoretical scattering spectra have been computed together with near- and far-field electromagnetic field distribution for each TE or TM polarization using COMSOL Multiphysics. Experimentally obtained and theoretically computed data are shown in Figure 1a and 1b for nanodiscs. We observe in TE polarization a single resonance, which exhibits a redshift for increasing diameters. This mode corresponds to a plasmon associated with a horizontal dipole ( $H_D$ , see illustration in Figure 1b), for which a spectral redshift with larger diameters is predicted by the plasmon theory and is linked to the lowering of the restoring force exerted on free electrons at the surface of the particle<sup>6</sup>. The experimental spectra are in excellent agreement with simulation. Experimental far-field images (see Figure 1c) also show similarities with the calculated radiation patterns. In comparison, gold nanocones exhibit intense plasmon resonances under TM illumination, corresponding to the excitation of a vertical dipole with large aspect ratio. Far-field optical images and experimental scattering spectra are shown in Figure 1d, together with numerical calculations. The dimensions used in the numerical modelling fit the experimentally obtained dimensions to an accuracy within a few percent.

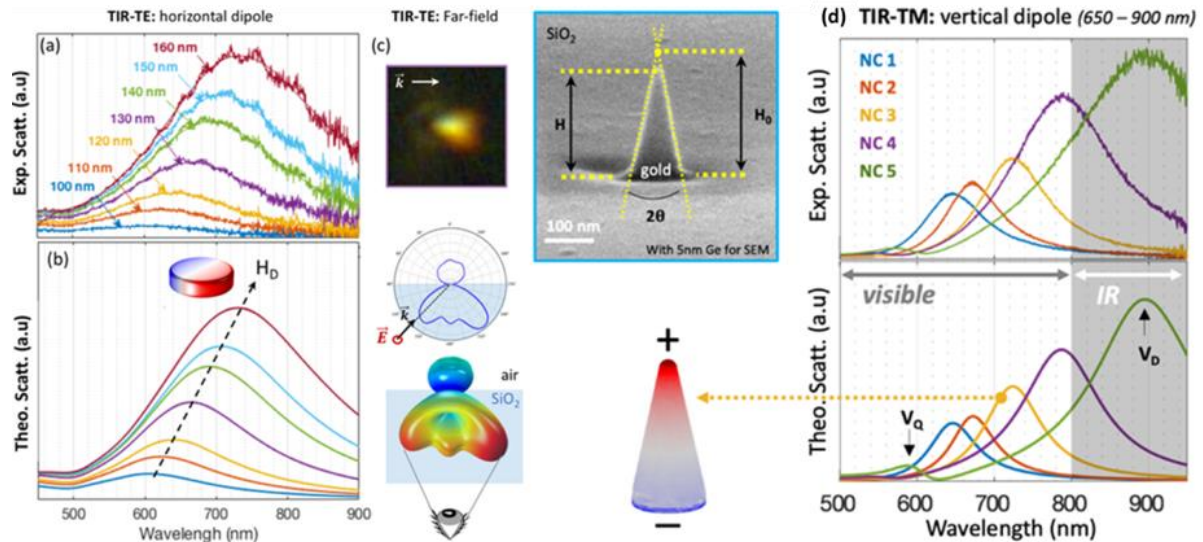


Figure 1. (a) Experimental TIR-TE scattering spectra for a series of individual Au nanodisks as a function of their base diameter (colors are used in the rest of the figure to label for the nanodisks diameters). (b) Corresponding calculated TIR-TE spectra, showing a horizontal dipole (HD) resonance sketched in the inset. (c) Far-field image of a single Au nanodisk (top) of 130 nm diameter, and radiation patterns of the HD mode in the plane normal to the air/glass interface (middle), and in a three dimensional representation (bottom). (d) Experimental TIR scattering spectra recorded (top) and calculated (bottom) for a TM optical excitation. Data for nanocones NC1-NC5 are shown in (a) and exhibit dipole resonances in the 500 nm-900 nm wavelength range.

### 3. Conclusions

To conclude, we fabricated nanostructures (gold nanodisks or nanocones) and measured their scattering spectra under TIR illumination. These spectra show clear and spectrally tunable resonances associated with local surface plasmons and are in excellent agreement with numerical modeling. Such tips will ensure high field enhancement factors together with a controllable spectral tunability as a function of the plasmonic material, size, and geometry. This work leads to the fabrication and characterization of fully designed nanoantennas dedicated to TERS measurements.

### 4. Acknowledgments

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