Spectroscopic characterization of lithographic metal nanostructures for tip-enhanced spectroscopic methods

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Summary
The optical plasmonic properties of metallic nanodiscs and nanocones have been characterized here—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 transverse electric and transverse magnetic plasmonic resonances are identified and observations are in excellent agreement with numerical simulations. The modelled and measured plasmonic response of the nanostructures suggests 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 tips. Such tips would enable a spectral tunability as a function of the specific material, the size, shape and topography, together with high electric field enhancement factors. Tip performances better than those commonly used in tip-enhanced optical spectroscopy experiments such as tip-enhanced Raman spectroscopy (TERS) are anticipated

1. Introduction

Accessing the optical spectroscopic properties of molecules and nanostructures with a spatial resolution less than the diffraction limit of the employed 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)[1], *which* can be used for concurrent chemical and physical surface mapping with a nanoscale spatial resolution[2]. 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 tip also govern the spatial resolution of the technique. In the case of TERS, the amplification factor (typically obtainable in the range of 10^4 to 10^8)[3] 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 a resist *lift-off* mask obtained using electron beam (ebeam) lithography[4-5]. 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 a single resonance in TE polarization, which exhibits a redshift for increasing nanodiscs diameter. 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[6]. The experimental spectra are in excellent agreement with simulations. 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. They have been measured here under TM conditions. Far-field optical images and experimental scattering spectra together with numerical calculations are shown in Figure 1d. The dimensions used in the numerical modeling, given by SEM observations, fit the experimentally obtained dimensions to an accuracy within a few percent.

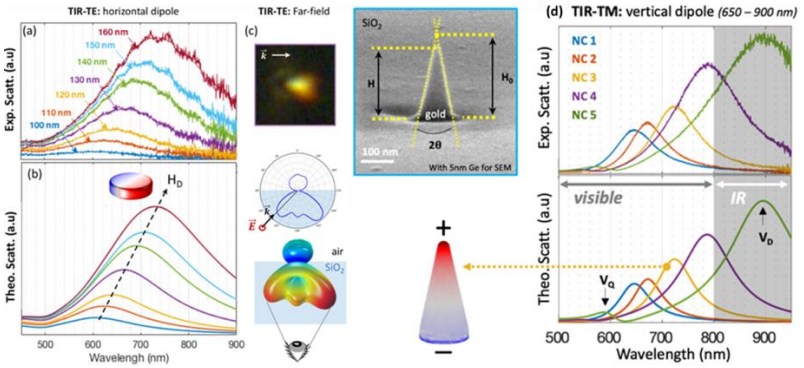

Figure 1. (a) Experimental TIR-TE scattering spectra for a series of individual gold nanodiscs as a function of their base diameter (different colours represent nanodiscs diameters). (b) Calculated TIR-TE spectra showing a horizontal dipole (HD) resonance indicated in the inset. (c) Far-field image of a single gold nanodisc (top) have a 130 nm diameter, radiation patterns of the HD mode in the plane normal to the air/glass interface (middle), and 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

We fabricated nanostructures (gold nanodiscs and nanocones) and measured their TIR scattering spectra under TIR illumination. These spectra show clear and spectrally tuneable resonances associated with local surface plasmons and are in excellent agreement with the predictions of numerical modeling. In the context of tip-enhanced opical scanning methods, our results suggest 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 nanostructures dedicated to TERS measurements.

4. Acknowledgments

This work has been supported by ANR “TIPTOP_1” (Project-ANR-16-CE09-0029).

5. Bibliography

[1] Anderson, M. S. Locally Enhanced Raman Spectroscopy with an Atomic Force Microscope. *Appl. Phys. Lett.* **2000**, *76* (21), 3130–3132.
[2] Kumar, N.; Zoladek-Lemanczyk, A.; Guilbert, A. A. Y.; Su, W.; Tuladhar, S. M.; Kirchartz, T.; Schroeder, B. C.; McCulloch, I.; Nelson, J.; Roy, D.; et al. Simultaneous Topographical, Electrical and Optical Microscopy of Optoelectronic Devices at the Nanoscale. *Nanoscale* **2017**, *9* (8), 2723–2731.
[3] Pettinger, B.; Schambach, P.; Villagómez, C. J.; Scott, N. Tip-Enhanced Raman Spectroscopy: Near-Fields Acting on a Few Molecules. *Annu. Rev. Phys. Chem.* **2012**, *63* (1), 379–399.
[4] Arscott, S. On evaporation via an inclined rotating circular lift-off shadow or stencil mask. *Journal of Vacuum Science & Technology B.* **2019**, 37 011602-12
[5] Eschimese, D.; Vaurette, F.; Troadec, D.; Leveque, G.; Melin, T.; Arscott, S. Size and shape control of a variety of metallic nanostructures using tilted, rotating evaporation and lithographic lift-off techniques. *Scientific Reports* **2019**, 9 7682-9.
[6] Langhammer, C.; Schwind, M.; Kasemo, B.; Zorić, I. Localized Surface Plasmon Resonances in Aluminum Nanodisks. Nano Lett. **2008**, 8 (5), 1461–1471.