## Surface Chemical Imaging at the Nanoscale

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The fields of Plasmonics, Raman spectroscopy, and Atomic Force Microscopy experienced a huge but independent development in the last decades. While AFM, in the past decade, has reached very high spatial resolution, but no chemical sensitivity, Raman spectroscopy has proven to be a very specific technique, although not highly efficient because of the low scattering cross-section. The potential progress derived by unifying these different techniques is of primary importance for obtaining simultaneous and complementary information at the level of single molecule detection [1], pioneering a new route towards the investigation of complex biological systems in a native environment and in label-free conditions. Here we propose and demonstrate that the convergence of such different methods can open access all at once to topographic, chemical and structural information on a spatial scale of few nanometers.

We report on the design, fabrication and measurements of a photonic-plasmonic device that is fully compatible with atomic force microscopy and Raman spectroscopy. It consists of a polystyrene micro-bead mounted on an AFM cantilever (see figure 1 and figure 2). The micro-bead acts as a perfect spherical lens able to focus the incident radiation on the base of the nanocone. When illuminated with radially polarized laser beams, it allows efficient electromagnetic coupling between the incoming laser and the nanocone. Surface plasmons, excited at the cone's base, propagate toward the tip where the electric field is adiabatically compressed in a region of few nanometers, producing a localized highly enhanced field [2]. The silver nanocone is fabricated by means of Focused Ion Beam milling and Electron Beam Induced deposition [3]. The commercial polystyrene micro-bead is mounted on an AFM cantilever employing Optical Tweezers manipulation, and then refined (grating) by means of Focused Ion Beam milling.

In addition to the fabrication results, we present theoretical design and Finite Difference Time Domain calculation of the device (figure 3). AFM surface topography was performed and compared to that obtained with a commercial tip, and chemical sensitivity with a spatial resolution up to 7 nm was demonstrated, thus setting a new benchmark for chemical analysis in label free conditions and physiologically friendly environments.

- [1] F. De Angelis et al., Nature Nanotechnology, 5 (2010), 67-72
- [2] F. De Angelis et al., *Optics Express*, 19 (2011), 22268-22279.
- [3] F. De Angelis et al., *Nanoscale*, 3 (2011), 2689-2696.

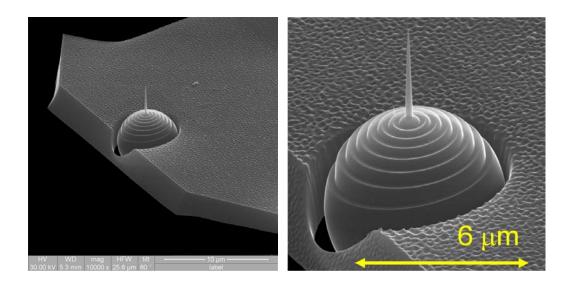


Fig.1 – SEM images of the device.

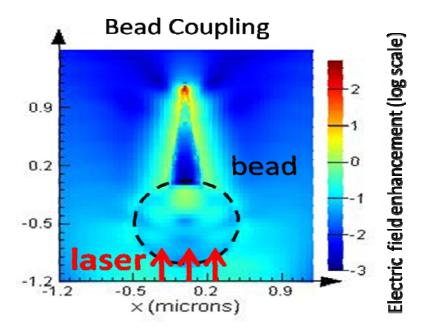


Fig.2 – FDTD simulation of the device. The micro-bead acts as a perfect spherical lens able to focus the incident radiation on the base of the nanocone.