Supplementary Information

Hybrid plasmonic-photonic nanodevice for label-free few molecules detection

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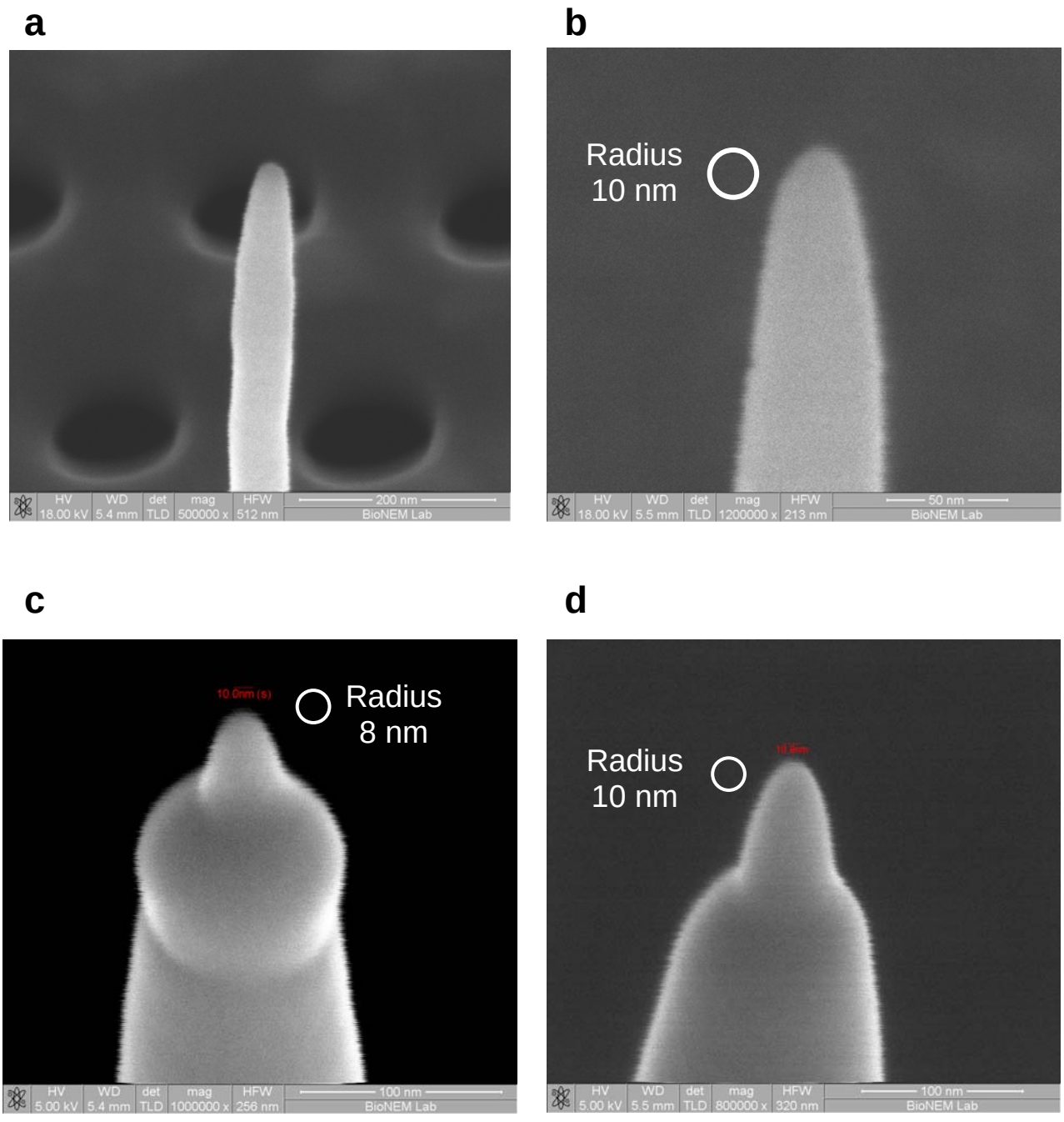
1. Plasmonic nanoantenna.

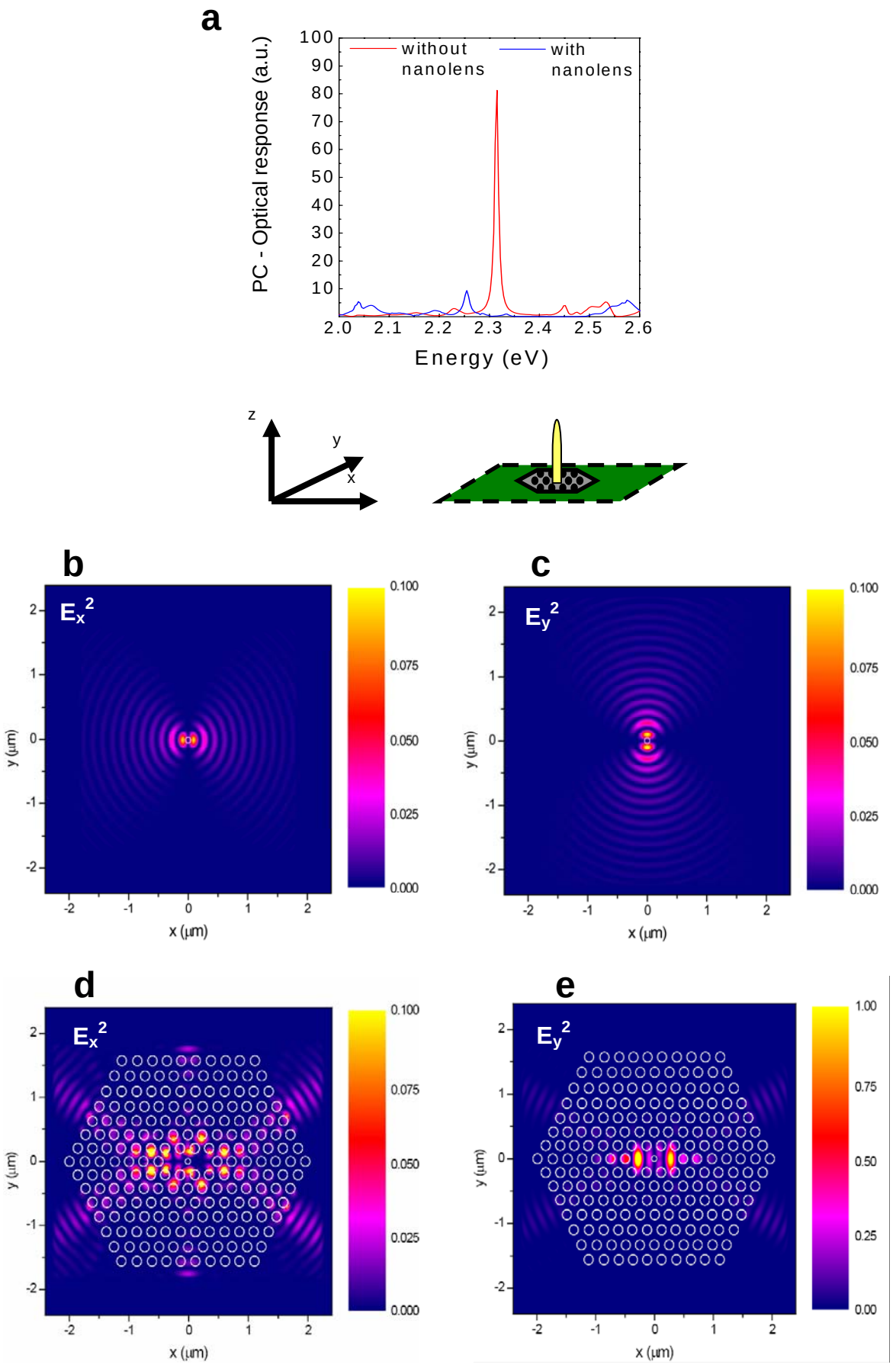
SEM images of gold tips of different nanoantennaes. In panel **a,** the tip with the Photonic Crystal (PC) on the background is shown, while in panel **b**, a detail of the tip with an higher SEM magnification ($1.2*10^6$) is shown. A radius of curvature of less than 10 nm can be clearly estimated. Panels **c** and **d,** show our present fabrication capabilities.



2. Design and optical response of the overall device.

The PC structure of the L3-type cavity is designed by a guided-mode expansion method. Dealing with an isolated cavity, we consider only TE-like modes for which the triangular lattice has a photonic band gap in all directions. Also, we further exploit mirror symmetry (for the isolated PC cavity and for the cavity with the nanoantenna) related to reflection with respect to the vertical bisecting plane. Then, the SPP optical response of the actual device is simulated by using a FDTD (Finite Difference Time Domain) code. Its algorithm is supplemented with the CPML (Convolution Perfectly Matched Layers) absorbing boundary conditions[25] and the Drude-Lorentz model for Gold (with plasma frequency $\hbar\,\omega_p$ = 8 eV and broadening $\Gamma = 0.015\ \omega_p$) that models the optical response of the nanoantenna material. The 3D computational domain is divided into 224×276×107 cells. The volume of each cell is 15.6×15.6×11.1nm^3. This cell size allows us a simulation of a tip radius of curvature of 20 nm at best. Such a spatial resolution gives rise to the step in time of 0.248×10^{-16} seconds. A modulated Gaussian pulse covering the spectral range 2.2 - 2.45 eV is emanated from a point source situated at the centre of the cavity just below the basis of the metallic nanoantenna. The detector is situated just above the PC cavity or above the tip of the nanoantenna depending on simulation conditions.

Notice that the color scale maps in figure are in arbitrary units but the numerical values reported are in the correct relative intensity values. The adopted reference system x,y,z is sketched for clarity in the centre of figure. **a,** FDTD calculation of the optical response of the PC cavity (the source is placed below the PC membrane and the detector is just above the membrane plane) in the photonic stop band region (2.2-2.5 eV) evidencing the fundamental cavity mode (red line) as compared to that of the PC cavity with the plasmonic nanoantenna on top (blue line). **b and c,** E_x^2 and E_y^2 spatial 2D profile (in arbitrary units) in the xy plane of the bare plasmonic nanoantenna on a Silicon Nitride membrane calculated at λ=514 nm. **d and e,** E_x^2 and E_y^2 spatial 2D profile (in arbitrary units) in the xy plane of plasmonic nanoantenna on the PC cavity calculated at λ =514 nm. These results confirm the concentration of the e.m. field operated by the PC cavity at the resonance frequency (notice the different color scale in the lower right panel).

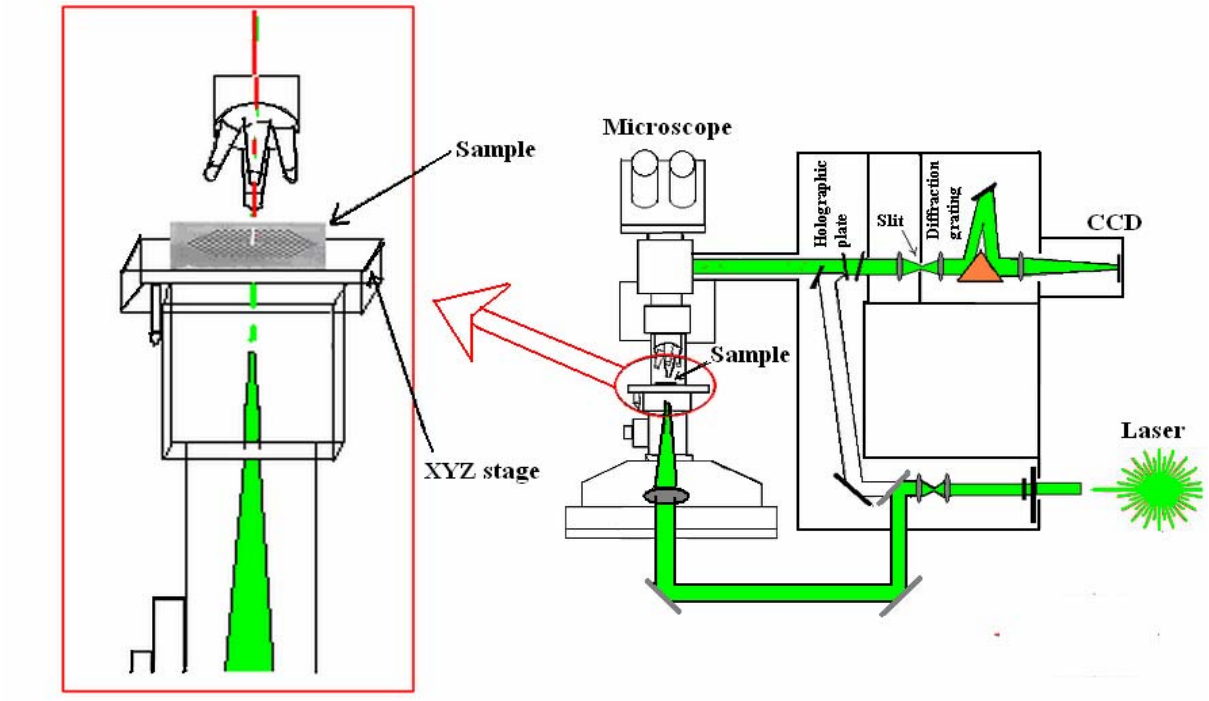

a
PC - Optical response (a.u.)
Energy (eV)
without nanolens
with nanolens
z
y
x
b
E_x^2
c
E_y^2
d
E_x^2
e
E_y^2
x (μm)
y (μm)

3. Experimental Raman Scattering setup.

Detailed setup for Raman Scattering experiments in transmission geometry (inVia Renishaw, 2006). The device is mounted on the microscope stage that allows very fine control of the nanoantenna position with respect to the microscope objective. The resolution of the piezo-electric positioning system of the stage is 100 nm in all x,y, and z axis directions.

The sample is illuminated from the bottom of the nanoantenna and PC cavity by unpolarized laser beam at 514 nm wavelength and power 0.18 mW. The collection of the Raman scattering signal is done in transmission with a direct microscope using 150X objective (NA - 0.95) with accumulation time (T_{int}) of 150 seconds.

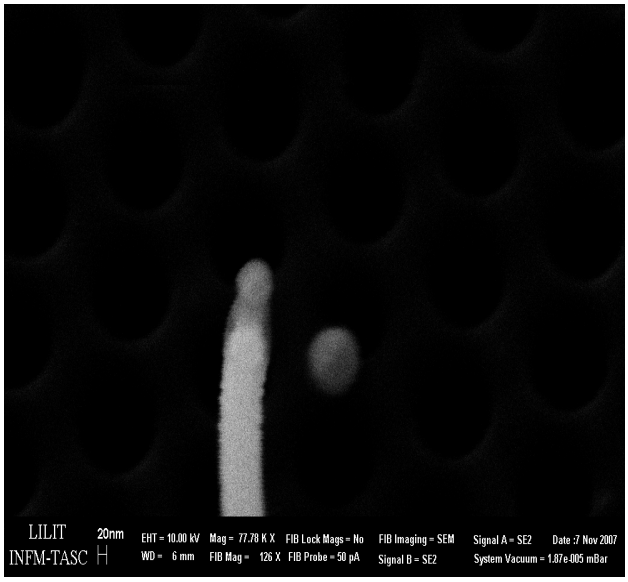
Confocal Raman measurements are performed for all samples described in this paper, namely, for SiOx, QD, and BTH monolayer. Moreover, Raman measurements on nanoantenna only (no PC cavity) are also performed.



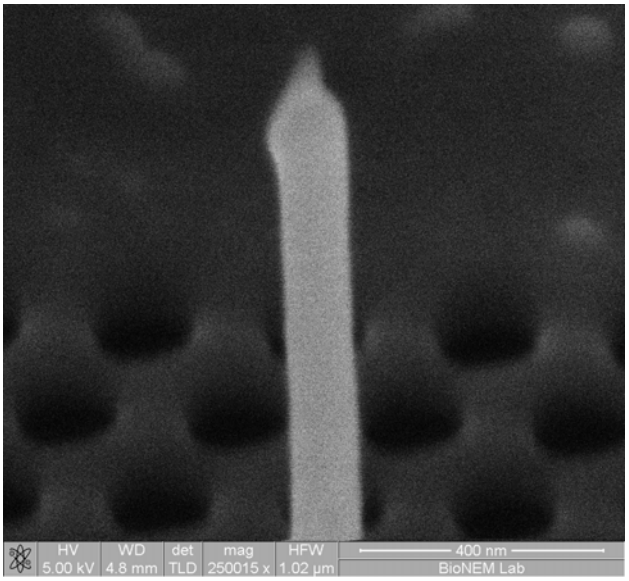
4. SiO_x deposition on nanoantenna.

SEM images of the tip of different nanoantennas after the deposition of SiO_x.The deposition of SiO_x is done by using electron beam induced deposition from the precursor gas TEOS (tetraethylorthosilicate). The SiO_x nanoparticle is selectively deposited in a specific position by focusing and positioning the electron beam, with nanometer precision with aid of a dedicated software. The electron beam is "on" for few seconds in the presence of a stationary flow of precursor gas. SiO_x is deposited, for each sample, at three different positions: **a,** at the apex; **b,** near the apex; **c,** along the wall of the nanoantenna. **d,** A thin layer of carbon is overgrown on nanoantenna surface during SiO_x deposition. **e**, SEM image showing a carbon layer purposely overgrown after 3 minutes of exposure without the SiO_x gas precursor, but with residual air in the SEM chamber.

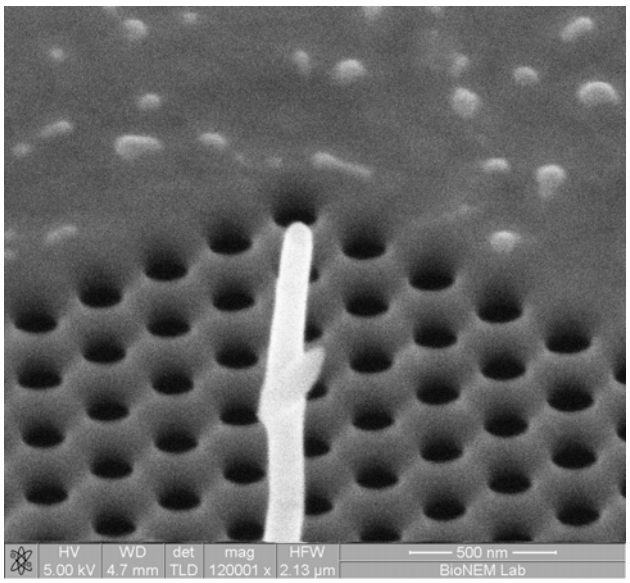
a



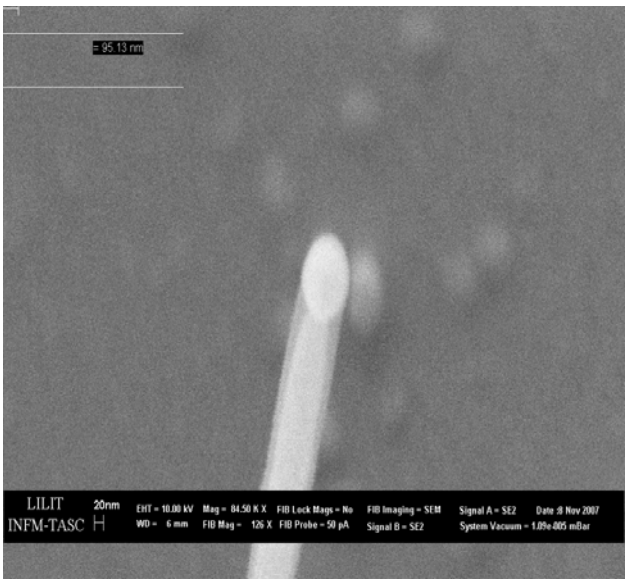
b



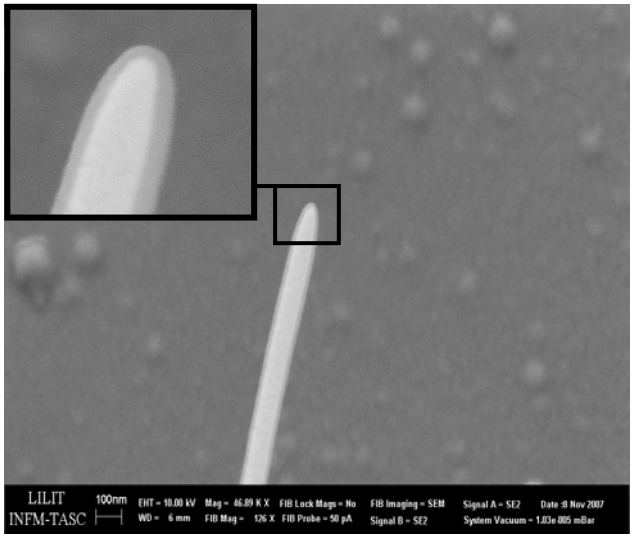
c



d

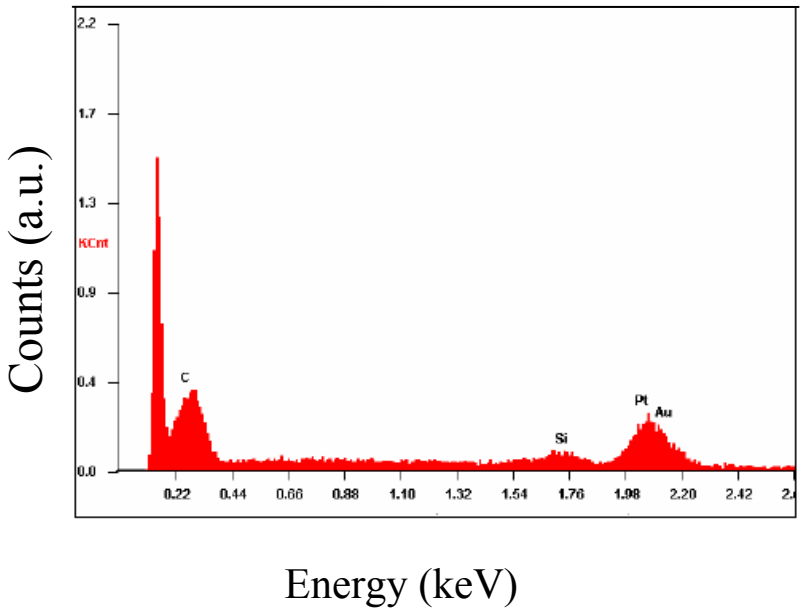


e



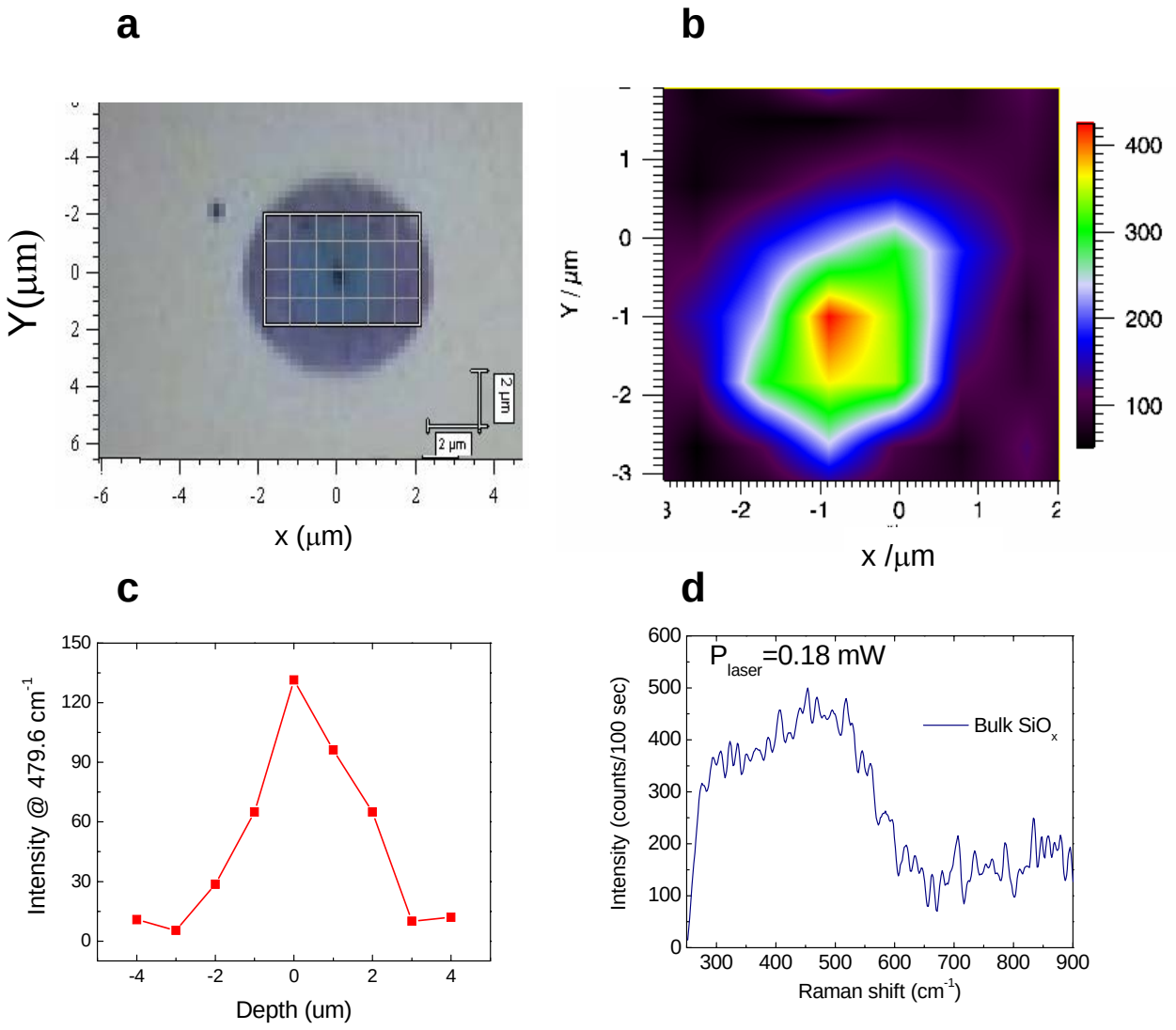
5. Micro-analysis of the nanoantenna.

X-ray micro-analysis spectra of the fabricated nanoantenna. The analysis clearly reveals the presence of Platinum/Carbon deposited from the gas precursor, and the presence of Gold covering the nanoantenna. To be noted the residual presence of Carbon co-deposited with Platinum, also detected in enhanced Raman Scattering measurements.



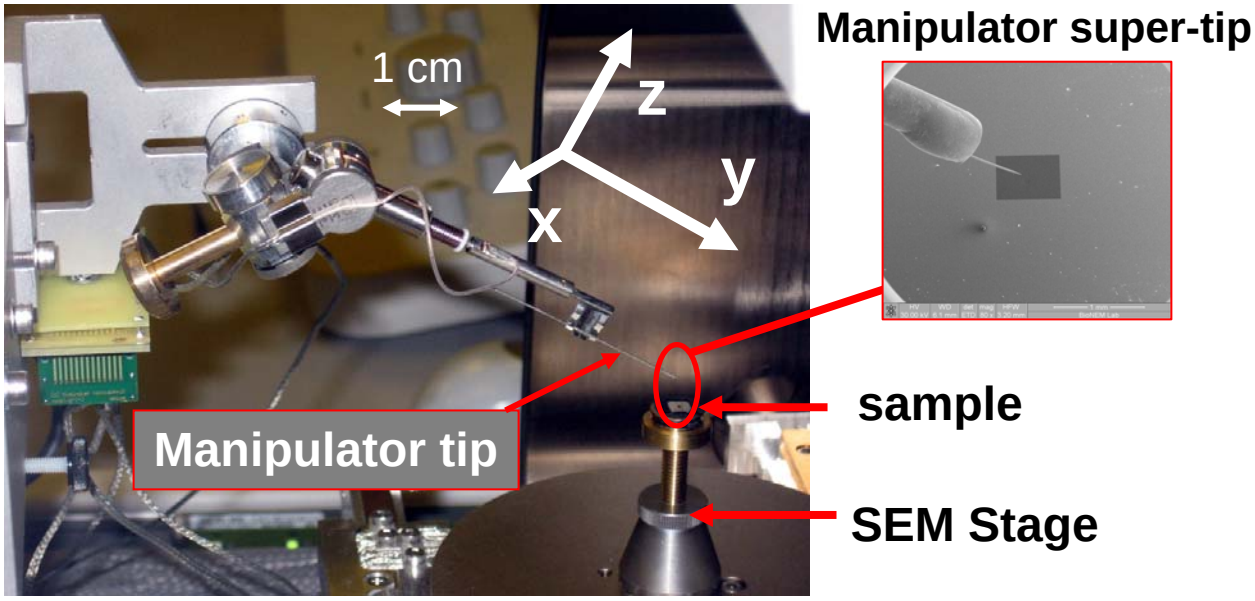
6. Raman Scattering measurements on SiO_x nanoparticles deposited on nanoantenna.

Raman Intensity mapping and maximization: **a,** Optical image of the PC cavity when performing the 2D map of Raman Scattering intensity at defined wavelength. **b,** 2D map of Raman Scattering intensity at λ=479.6 cm^{-1} as measured on the SiO_x nanoparticle deposited at the nanoantenna tip apex in S1 configuration (see text). **c,** z-scan of the Raman Scattering intensity at 479.6 cm^{-1}, as measured along the nanoantenna for a total scan range of 6 μm in S1 configuration. **d,** Raman Scattering spectrum of a SiO_x bulk sample on gold coated Silicon Nitride membrane, deposited at the same experimental condition of SiO_x nanoparticles.



7. Nanomanipulator.

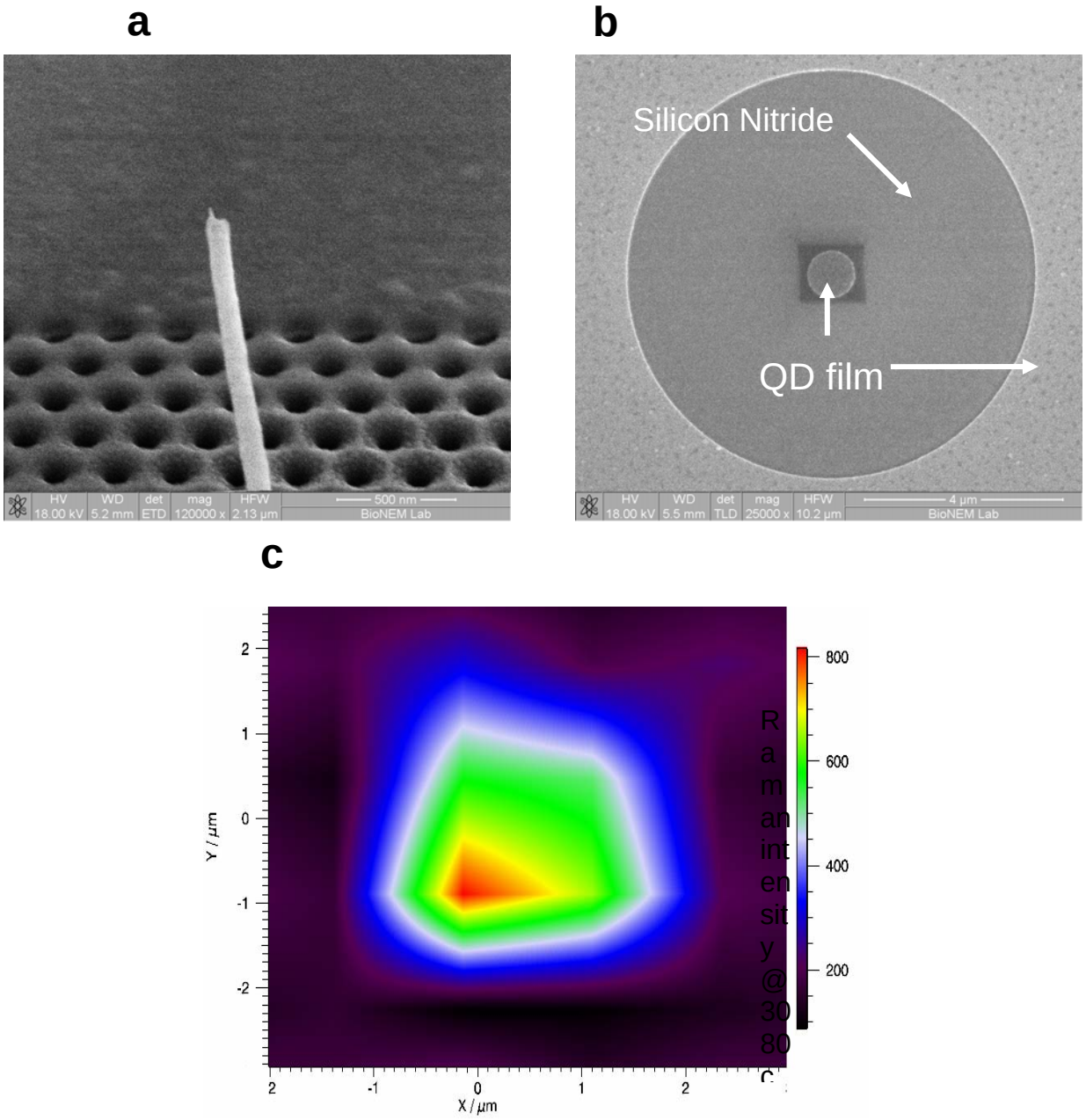
The Nanomanipulator mounted in the SEM vacuum chamber; in the inset a SEM image of the manipulator tip over the sample. The tip positioning system is controlled by piezoelectric motors with 3 additional degrees of freedom with respect to the SEM stage as indicated in the picture (Z: out-of-plane rotation, resolution=5 nm; X: in-plane rotation, resolution=3.5 nm; Y: tip axial shift, resolution=0.25 nm).



8. Raman Scattering measurements on QD samples.

a, SEM image of a nanoantenna with few QDs deposited at the apex. **b,** SEM image of a definite volume of QDs spinned on a Silicon Nitride membrane. After the spinning the sample is patterned in order to obtain a definite QDs volume, (a cylinder of 1.2 μm diameter and 200 nm in height). **c,** 2D map in the xy plane of Raman Scattering intensity at 3080 cm^{-1} as measured on the QD on nanoantenna.

The sample in **b** allows us to obtain a direct evaluation of the enhancement factor (that results to be about 10^5) in bleaching conditions. For these QDs the fluorescence is bleached after 2 minutes under laser exposure at power density equal to 2.7 KW/cm^2 , as obtained for single QD[1].



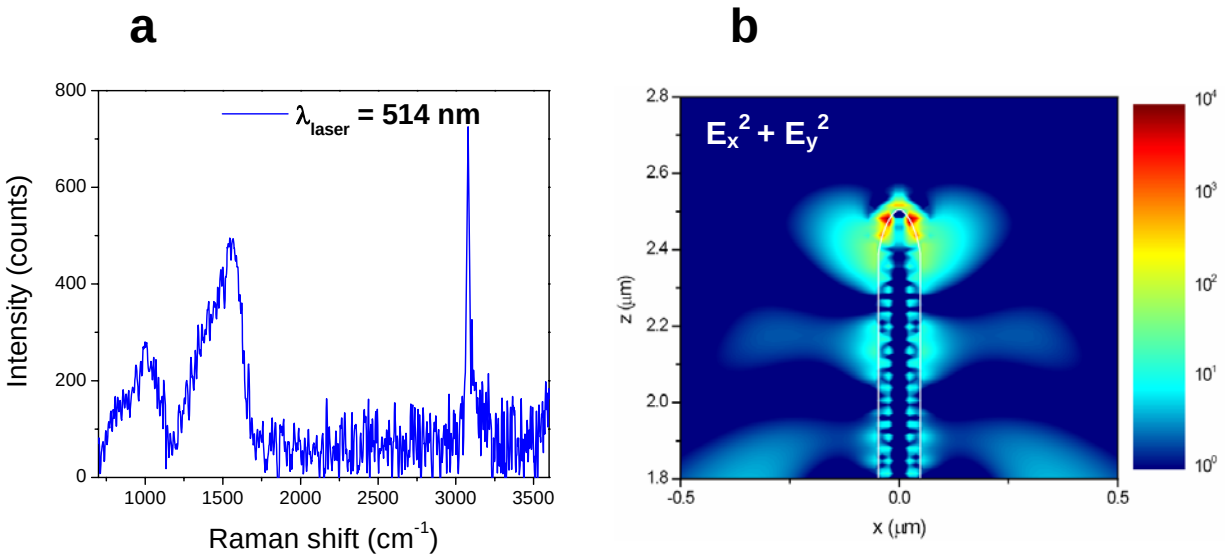
[1] Lee S.F. and Osborne M.A., *J. Am Chem. Soc*. **129**, 88936 (2007)

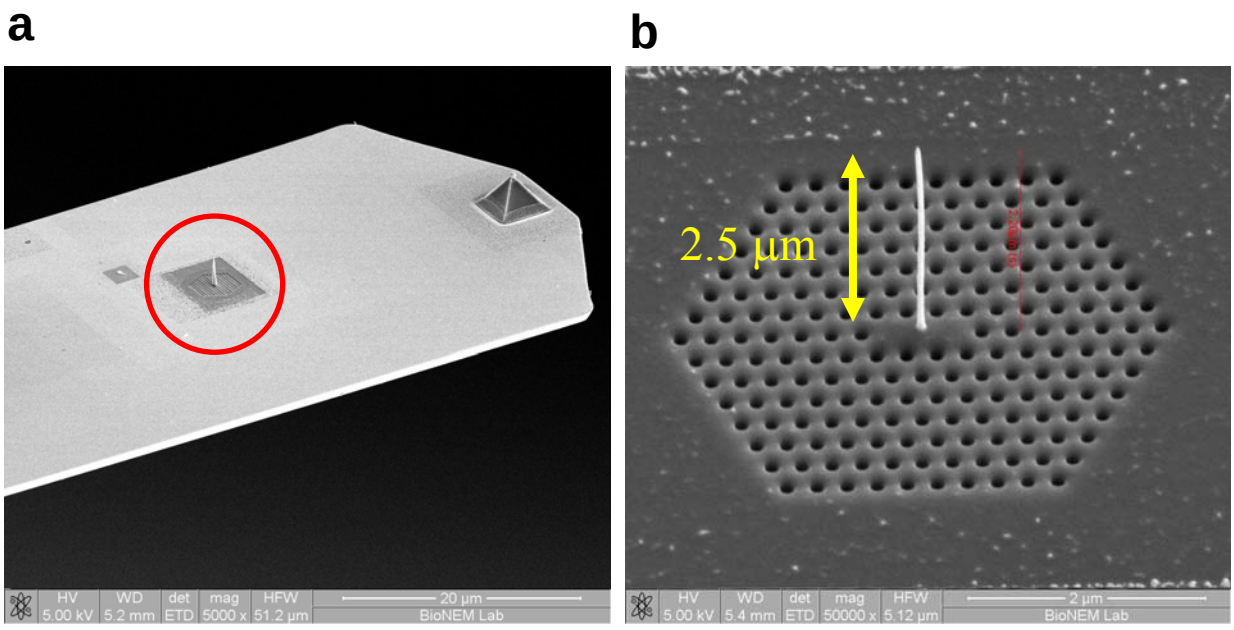
9. Raman Scattering measurements on single QD on nanoantenna, and FDTD simulation.

a, Raman scattering spectra of single QD deposited at nanoantenna tip (P=0.18 mW, T=150s) excited at resonance wavelength, λ=514 nm

d, 2D map of FDTD simulation of $E^2 = E_x^2 + E_y^2$ along the nanoantenna, on resonance at λ_{exc}=514 nm,.

These results confirm the strong enhancement of the e.m. field intensity at the tip at the resonance frequency (notice the different color scales): the ratio between resonant and non-resonant condition is by a factor of 10^2-10^3, depending on exact position.



10. SENSe on Atomic Force Microscope cantilever.

a, Overview of an AFM cantilever with the PC cavity and plasmonic nanoantenna fabricated on its surface. The silicon nitride cantilever is locally thinned on one side in order to obtain a membrane thickness of 100 nm necessary for the fabrication of the desired a PC cavity. The local thinning of the membrane doesn't affect the mechanical properties of the cantilever. The aim of this architecture is to combine Atomic Force Microscope and Raman Scattering technique. The performances of such nanoantenna as AFM super-tip has been tested by the authors to obtain AFM setup topography images in wet conditions (the images can be supplied upon request to the authors). In the next future the AFM will be combined to Raman Scattering spectrometer. **b,** Details of the PC cavity and nanoantenna. The fabrication quality is comparable to that obtained on a Si_3N_4 membrane.