## Breaking the diffusion limit of nanosensors through super hydrophobic and nano plasmonic structures

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The detection of few molecules from highly diluted solution is of extreme interest in different fields such as biomedicine, safety and eco pollution from rare and dangerous chemicals. Nanosensors based on plasmonic structures are promising devices that combine high sensitivity, label free detection and miniaturization [1]. However, plasmonic based nanosensors, and more in general sensors whose sensitive area is in the nanometer scale, cannot directly be used for detecting molecules dissolved in femto/atto molar solutions. In other words, they are diffusion limited and their detection time becomes unpractical at those concentrations. In this work we demonstrate that few molecules can be localized and detected even at atto molar ( $10^{-18}$  mole/litre) concentration.

The basic idea is to exploit super-hydrophobic surfaces to drive molecules toward those positions where nanosensors are placed. Molecules of interest, initially dispersed in solution of few  $mm^3$  in volume, are guided toward the active area of the sensors with an accuracy of few  $\mu$ m. An example is shown in figure 1. We designed and fabricated a plasmonic nanosensor in the barycentre of the hydrophobic surface (figure 2), and we were able to observe a detailed Raman signature of less than 10 molecules of lysozyma starting from 1 fM solution. In our knowledge, this is the lowest number of molecules from 1 fM concentration solution ever detected by physical methods. This work faces radically the "diffusion limit" and proposes a way out to treat highly diluted samples.

Moreover, by varying the dilution is possible to create a suspended regular  $\lambda$ -DNA network (figure 3). In the next future, the possibility of having isolated suspended DNA, or more in general elongated macromolecules, will allow novel biochemical and physical insights.

[1] [1] F. De Angelis et al., Nature Nanotechnology, 2010, 5, 67-72.[2] F. De Angelis et al., Nature Photonics, 2011, 5, 682-687.



Figure 1. On the left: optical image of the device showing the initial drop and final residue. On the right: SEM image of the residue concentrated over the surface of silicon pillars.



Figure 2. Silver nanocone placed in the center of hydrophobic array: it acts as a defect that lowers the hydrophobicity and attracts the molecules dispersed in solution. At the same time it works as a plasmonic nanolens enabling few molecules detection.