Nanoplasmonics 2:

Location Specific Sensing in Plasmonic Nanowells

In this application example, it is shown how specially tailored nanostructured plasmonic substrates can provide a means for location specific sensing. By fabrication of nanowells, surfaces with 'negative curvature' are introduced, mimicking e.g. the inside of a vesicular membrane. Location specific nanoplamonic sensing allows distinguishing between the response from biomolecular interactions inside the wells from the in-between planar regions.

Surface Plasmon Resonance (SPR) has emerged as the standard method for biomolecular interaction analysis. As an alternative to standard SPR technology, Nanoplasmonic sensing (NPS) further enables exploration of the influence of nanostructure on bio-molecular interactions. By purposeful tailoring of the nanostructured plasmonic elements it is possible to introduce both convex and concave features with various radii.

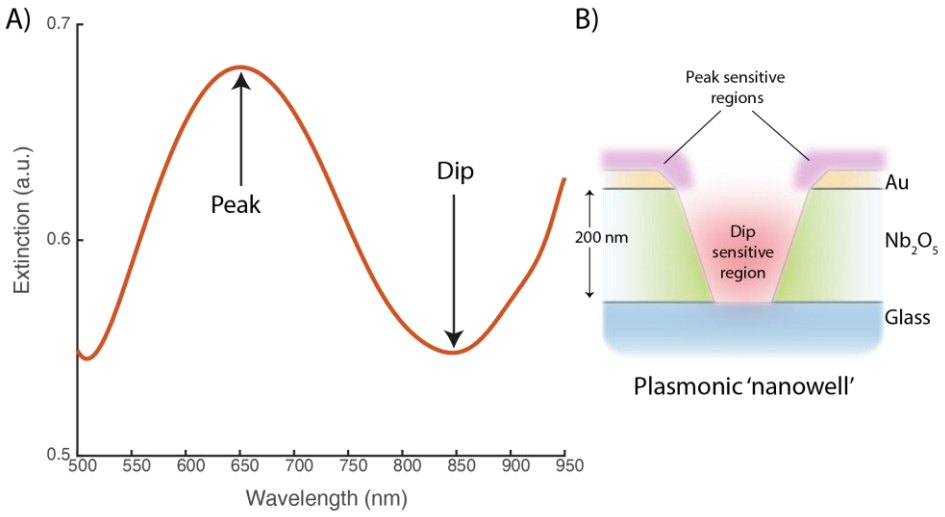

Figure 1: A) The extinction spectrum of the plasmonic nanowells exhibits a plasmon resonance peak and dip. B) Schematic representation of the nanowells.

In this application example, a nanostructure consisting of 'plasmonic nanowells' (Fig. 1B) is used to create a surface with 'negative' curvature. Interactions at biological surfaces with negative curvature are especially difficult to study using other methods because e.g. the interior of a lipid vesicle is generally inaccessible. However, such surfaces are of considerable interest since geometry plays an important role in many biological processes.
The nanowells used in this study were made of holes in two thin films consisting of gold and niobia (Nb_2O_5) and were fabricated by colloidal lithography. The wells were 100 nm in diameter, and the gold and niobia film 30 and 200 nm thick respectively.
These nanowells exhibits both a plasmon peak and a dip in the extinction spectra (Fig. 1A). The spectral position of these features is highly sensitive to the local dielectric environment. The peak corresponds to a propagating plasmon mode in the gold film while the dip is associated with a localized surface plasmon in the nanowell. Therefore, the peak is predominately sensitive to events in the regions immediately adjacent to the gold film, while the dip is most sensitive to the region inside the well. In this way, the plasmonic nanowell structure constitutes a location specific sensor enabling differentiation of binding events on the flat surface or within the well.

To demonstrate the location specific sensing effect nonspecific adsorption of the protein avidin was used.

Figure 2 A shows the change in resonance wavelength

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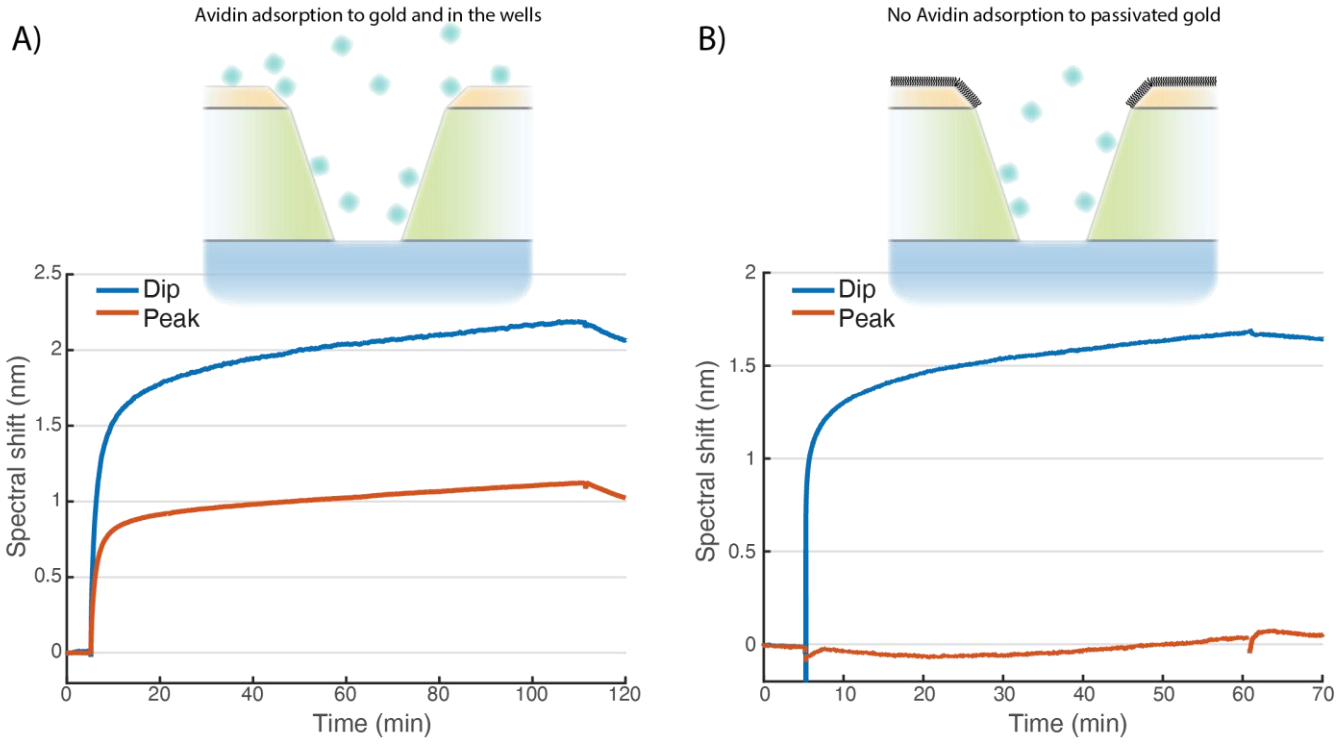

Figure 2: Shift in resonance wavelength for the dip (blue) and peak (red) upon direct protein adsorption (A) and selective protein adsorption within the wells (B).

upon direct adsorption of avidin for the Dip and Peak respectively. As can be seen the sensitivity is higher for the dip over the peak. This is expected due to the difference in refractometric sensitivity of the different plasmon modes. In Figure 2B, the planar gold areas have been passivated through selective chemical modification with an ethylene glycol terminated alkanethiolate self-assembled monolayer. This effectively blocks the planar gold areas from protein adsorption. As can be seen there is no spectral shift of the plasmon peak, while the dip exhibit a substantial signal, owing to the location sensitivity of the respective plasmon resonances.

By analyzing multiple parameters from the extinction spectrum of plasmonic nanowells it is possible to distinguish between signals caused by molecular binding to different locations of the substrate. This allows for example for studying the effect of negative curvature (the inside of the wells) on interactions between proteins and biological surfaces.

Note

This study was performed by Dahlin and coworkers at the Department of Applied Physics, Chalmers University of Technology, Sweden.

Juliane Junesch, Gustav Emilsson, Kunli Xiong, Shailabh Kumar, Takumi Sannomiya, Hudson Pace, Janos Vörös, Sang-Hyun Oh, Marta Bally, and *Andreas Dahlin.* Nanoscale **2015**. DOI: 10.1039/c5nr04208a.