Supporting information

Plasmon Enhanced Enzyme-Linked-Immunosorbent-Assay on Large Arrays of Individual Particles Made by Electron Beam Lithography

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Spectral fluctuation in the single particle measurements. The accuracy in the peak shift determination in the single particle measurements were estimated by scanning the same EBL particles 7 times in succession without any time delay between the scans. The peak position variations for 6 individual particles are shown in Fig. S1 a). The distribution of the fluctuations between each scan is plotted in Fig. S1 b). The standard deviation of this fluctuation is 0.1 nm. The co-variation observed between different particles indicate that the variation is mostly due to true fluctuations, for example due to random movements of the sample stage, stability of the light source etc., rather than signal limited shot noise.

This conclusion is supported by an analysis of how the actual spectral readout noise and shot-noise affect the accuracy of the peak position determination, which turns out to be better than 0.04 nm for the system parameters used.
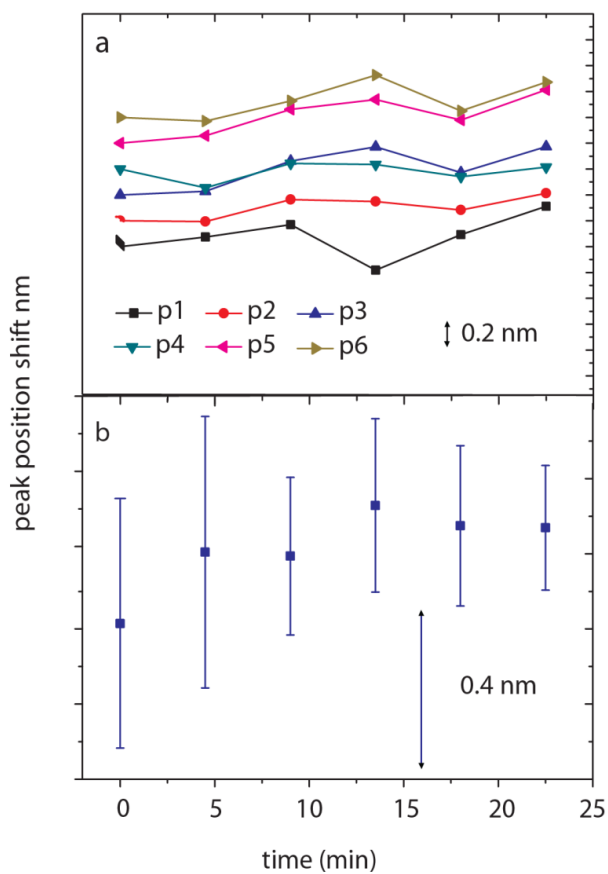

Figure SI1. a) Peak position fluctuations of a blank sample measured with LCTF visualized with 6 randomly chosen particles. b) Averages of peak position shifts for 300 different particles.

The electromagnetic response of the rods is simulated using the finite-difference time-domain (FDTD) method. Since the exact dimensions of measured rods are known only approximately (fabrication inaccuracies), we use the following lengths: long axis – 115 nm, short axis – 65 nm, height – 40 nm, rounding radius (according to SEM images) – half of short axis length which decreases with the height, side wall taper angle 10 degrees. The dielectric function of gold is based on measurements by Johnson and Christy.[1] The rod is placed on a substrate with a refractive index of 1.45 and is immersed in water (n = 1.33). This gives a long axis plasmon resonance at approximately 730 nm in accordance with the observed experimental peak positions.

The molecular precipitate is simulated as a dielectric sphere (we assume that the precipitation reaction is isotropic) with a refractive index of 1.45, a value that is in agreement with previous analysis and gives a similar saturation peak-shift at full coverage as measured in experiments. The center of the sphere is located at the surface of the rod at various probing positions and only displaces water. Thus, if it is located at the bottom of the rod at the center of the long side the actual shape of the precipitate is in fact close to a quarter-sphere, while at the top of the disk it resembles a half-sphere. This means that the "optical weight" of the sensed precipitate changes and further modifies the non-homogeneous response dependent on the "local" field enhancement (if the sensed object was always the same).

The FDTD simulations are performed using the commercial code FDTD Solutions by Lumerical Solutions, Inc. The minimum mesh size is 2 nm in a volume that encompasses the whole rod as well as all possible volumes occupied by the sphere. This ensures that the rod is always meshed in the same way and variations in meshing do not introduce any unnecessary uncertainties. The peak position is extracted from optical scattering data (extinction, scattering, absorption) in the spectral range 650-850 nm. The peaks are analyzed for the peak position (fitting and maximum identification).

The peak-shift map that we obtain is a spatial representation of the strength of the optical response induced by placing a dielectric sphere (precipitate) at a varying positions on the surface of the rod. To accomplish this we discretize the surface of ¼-th of the rod (due to symmetry) into a 10 by 10 mesh, as shown in Fig. SI2 (small blue spheres). We run FDTD simulations with a precipitate (transparent red sphere) placed at subsequent points (in Fig. SI2 a particular one is marked in red) to measure the peak-shift relative to a bare gold rod. Peak-shift maps for precipitates 13 and 25 nm in diameter are shown in Fig. 5 (insets in a and b). These plots are obtained from the raw data by interpolating to a finer mesh (for higher-quality plots) and smoothing. With light polarized along the long axis, hot spots are found at either end of this axis. This is made evident by the location of the largest observed peak-shifts. When the molecules are located at the top or one the sides of the rod, due to lower field enhancements the response of the plasmon is weak.
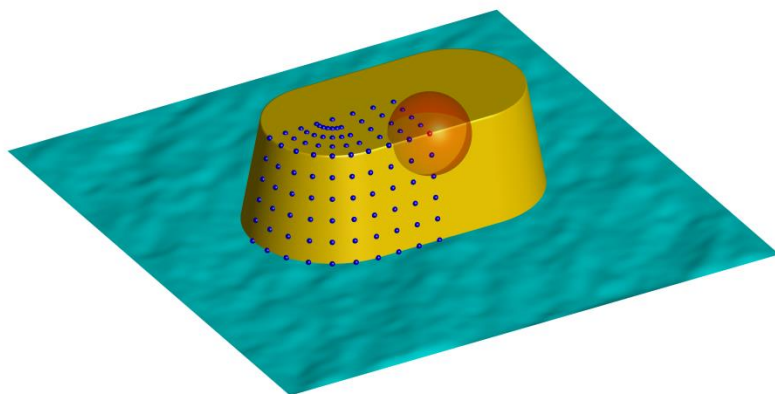
Figure SI2. Placement scheme of the molecular precipitate on the surface of a gold nanorod. A fourth of the surface (due to symmetry) is discretized into a 10-by-10 point grid as shown by the small blue spheres (some points overlap due to the curvature of the rod caps and ease of creating the map). In each of the 94 FDTD simulations we place a dielectric sphere (here, an exemplary one in red) at one of the grid points. The optical spectrum is calculated and compared to the reference one without the precipitate. The such-obtained peak-shift value is then used to create an interpolated peak-shift map that is presented in Fig. 5.

1.   Johnsson, P. B.; Christy, R. W., Optical Constants of Noble Metals. *Phys. Rev. B.* 1972, *6*. 4370-4279