For calculating the scattering properties of spherical gold particles, we used the multiple-multipole method<sup>1,2</sup> and the data of Johnson and Christy<sup>3</sup> for the dielectric function of gold. We considered spheres with diameters of 30 to 100 nm with a 10-nm increment. In accordance with the experiment, the particles were embedded in a medium with refractive index n = 1.52 and excited by a plane wave. Their backscattering properties were determined by integrating the resulting Poynting vector collected in a detection cone of 72° half angle (N.A. = 1.45).

In the graph below, the sphere diameter is plotted vs. the respective calculated resonance wavelength (black squares). We have chosen to present this inverse curve as the resonance wavelength is the value accessible in the experiment. The error bars represent the spectral step width of the calculation (1 nm abscissa error) and its propagation in the fit function (red curve)

$$d[nm] = \frac{171.35 \cdot \lambda_{res}[nm] - 91500}{\lambda_{res}[nm] - 478}$$



In order to verify the validity of modeling the grown particle as a sphere, we have calculated the scattering spectrum of a 3D spherical Au calotte as depicted in the Figure below. The calotte has a long diameter of 100 nm parallel to the substrate plane, and a short perpendicular one of 65 nm. The transition from the plane bottom surface to the spherical part of the surface has been smoothed with a radius of curvature of 10 nm (not shown in the sketch). Such a shape can certainly originate during the growth process due to the influence of the substrate. The comparison of the scattering spectrum with the one obtained theoretically from a 100-nm sphere clearly indicates that the resonance wavelength of both types of particles is found around 610 nm and within the error margin of our experiment for this particle size (~3 nm). This result shows that the diameter of the large axis of the particle is the crucial parameter for the spectral position of the LSP resonance wavelength, and that it is sufficient to account for this parameter in a spherical model.



(1) Hafner, C. *Post-modern Electromagnetics: Using Intelligent MaXwell Solvers*. John Wiley & Sons: Chichester, 1999.

(2) Hafner, C. MaX-1 A Visual Electromagnetics Platform for PCs. John Wiley & Sons: Chichester, 1998.

(3) Johnson, P. B.; Christy, R. W. Phys. Rev. B 1972, 6, 4370.