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Supplementary Information

Double-layered nanoparticle stacks for surface enhanced infrared absorption spectroscopy

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Removal of electron beam resist

Self-assembled monolayer formation on the surface of the metal nanoparticles requires complete removal of e-beam resist deposited on top of the cylindrical nanoparticles. A challenging task was to find removal settings for which the deposits wash off completely while geometry and disc shape are preserved.

We varied the duration of sample sonication in piranha solution and intermittently checked the resonance position via IR absorption measurements and the geometrical abrasion with scanning electron microscopic images. The optimal results were found at a duration of 6 h (sonicated

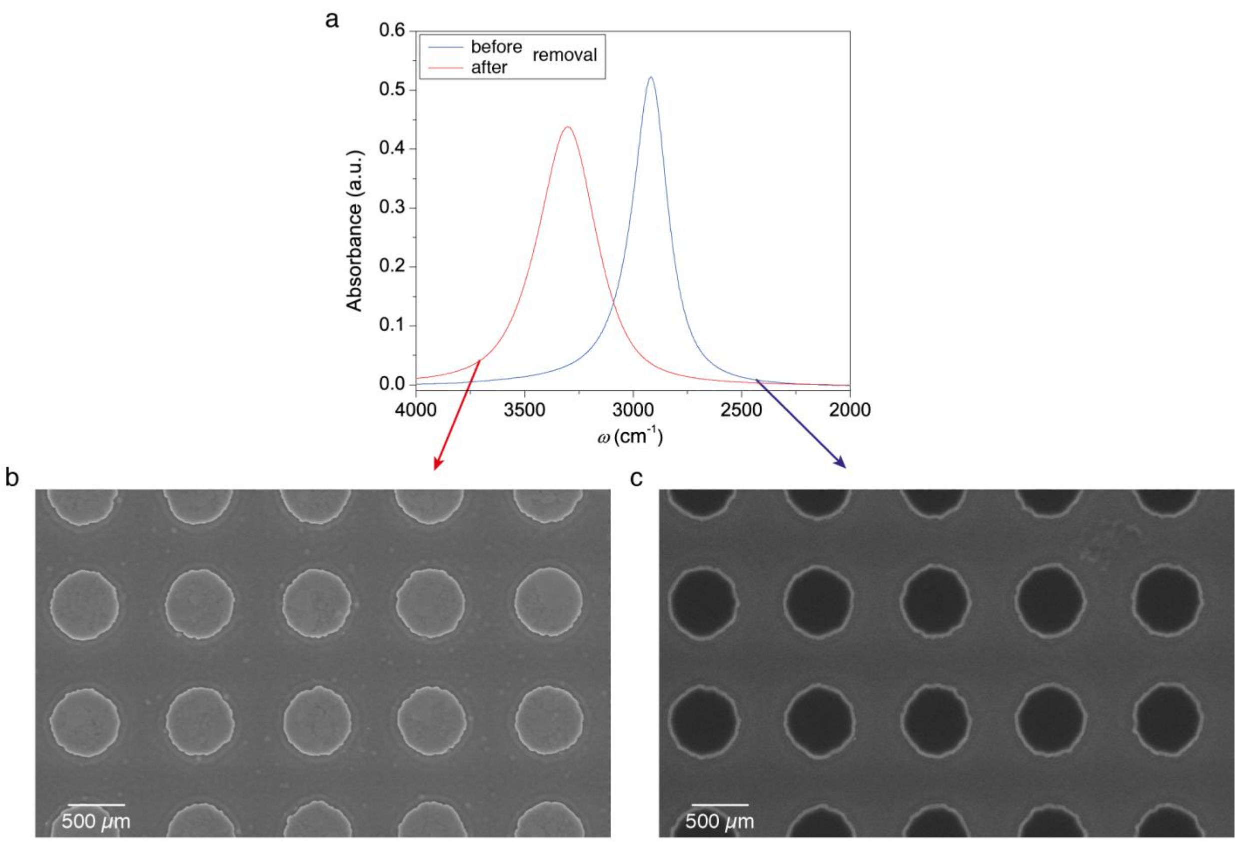

Figure S1. Preserving the structure while removing e-beam resist. (a) IR-spectrum of the plasmon resonance before and after removal of the e-beam resist. (b), (c) Scanning electron microscope images of the corresponding resonances show slight alterations of the geometry. E-beam resist deposits appear dark, due to their low conductivity.

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in an upright position) at 40 °C. An average blue shift of the plamonic resonance position of 387 ± 28 cm^{-1} was found for the change in the dielectric environment through removing the deposit (see Supporting Figure 1a). We found a broadening of the plasmon peaks of about 27 cm^{-1}, which we attribute to small aberrations especially at the edges of the particles (see Supporting Figure S1 b, c).

Diameter variations in fabrication process

The correlation between disk-stack diameters and plasmon resonance positions has been proved using infrared microscopy. Each of the 200 x 200 µm² disk-stack pattern was monitored using focal plane array detection of the infrared spectra. Figure S2 shows the direct correlation between the infrared absorbance and the drop in diameter of the stacks at the boundary of the array.

FDTD-Simulations

We performed three dimensional finite difference time domain (FDTD) simulations using the open source software MEEP.[1] A uniform mesh size of 3.33 nm in all dimensions was used. The optical parameters of Au were taken from Rakic and coworkers.[2] The refractive indices used for glass and Ta_2O_5 were 1.517 and 1.74, respectively. The simulated data represent perfectly arranged monodisperse disc-stacks for which an unambiguous relation between the stack diameter and the plasmon resonance position is revealed (see Fig.2b in the manuscript).

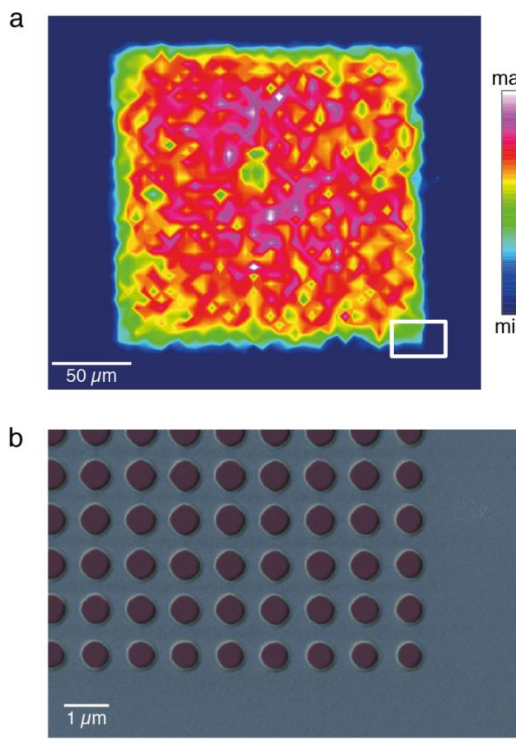

Figure S2. Focal plane array measurement of disc-stack array. (a) The two-dimensional map shows the intensity of the absorption at a frequency of 3020 cm^{-1} according to the plasmon resonance of this structure (disc-stack diameter: ~680 nm) with a spatial resolution of ~2.7 µm on a 200x200 μm^2 array. The lowered intensity at the borders of the array is attributed to a shift of the plasmon resonance due to a drop in the nanoparticle diameter. (b) Scanning electron microscope image (false color) shows a magnified view of the area in the white box in (a), with a clear decrease of the disc-stack diameter at the boundary of the grating.

References:

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2. A. D. Rakic, A. B. Djurisic, J. M. Elazar and M. L. Majewski, *Appl. Opt.*, 1998, **37**, 5271-5283.