Fabrication of plasmonic nanoantennas by femtosecond direct laser writing lithography - effects of near field coupling on SEIRA enhancement

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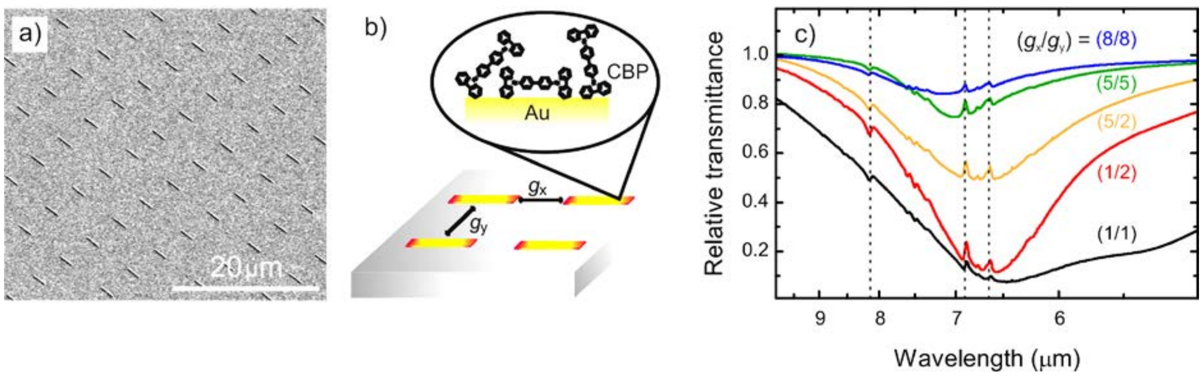
Infrared (IR) spectroscopy is a label-free and non-destructive method to identify and quantify molecular species based on their material specific IR absorption. Additionally, these characteristic vibrations, also known as infrared fingerprint, can be used to obtain information on the molecular configuration. It is therefore a well-established characterisation technique in physics, life science, and chemistry.
Unfortunately, infrared spectroscopy suffers from relative low absorption cross-sections of molecular excitations. One way to overcome this limitation is the use of specially designed metal structures, namely resonant plasmonic antennas. Such plasmonic structures concentrate electromagnetic radiation in nanometer-sized volumes and therefore provide large near field enhancements. Molecular vibrations of species located in these hot spots can be enhanced up five orders in comparison to conventional infrared spectroscopic measurements. However, most of these studies utilize geometries for surface-enhanced infrared spectroscopy (SEIRA) on small-area samples fabricated by e-beam lithography or other methods. To bring these advances into life science laboratories and allow for broad range applications, large-area, low-cost, fast and flexible fabrication is required.



Here we utilize femtosecond direct laser writing employing two-photon absorption in photoresist to fabricate plasmonic nanoantennas resonant in the near- and mid-infrared spectral range on cm^2-sized scales. We use the photolithographically patterned resist as etch mask to create nanoantennas in a gold film using argon ion beam etching. This method allows for reliable, easy, low-cost and large-area fabrication of nanoantenna arrays (see typical electron micrograph in figure 1a) for surface-enhanced infrared absorption. We demonstrate the fabrication of a wide variety of arrays and examine particularly the influence of plasmonic coupling between neighbouring antennas on the SEIRA enhancement effect. Therefore we prepared gold nanoantennas separated by different spacing in *x*- and *y*-direction as illustrated in figure 1b) and covered them with a 5 nm thick layer of 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) acting as a molecular probe. Beside the broadband plasmonic resonance, the relative infrared transmittance feature enhanced CBP vibrations (indicated by dashed lines) strongly depend on the separation g_x and g_y as shown for selected antenna configurations in figure 1c). After a baseline correction, we find that optimum SEIRA enhancement is achieved when the antennas are placed at lateral distances close to $g_y = \lambda_{res}/n$, in direction perpendicular to the long antenna axis, where λ_{res} is the resonance wavelength (transmittance minimum) and n the refractive index of the substrate.