

Enhanced infrared spectroscopy with optical antennas

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“Optical antennas” are nanostructures that concentrate light into nanoscale dimensions. They can be understood in analogy to conventional radio antennas, e.g. the well-known $\lambda/2$ dipole antenna that converts radiation into currents. Due to their much smaller sizes these optical antennas have resonance frequencies not at radio frequencies, but in the visible or infrared spectral range. If such an optical antenna is driven in resonance, the scattering, the absorption and the local field around the antenna can be dramatically enhanced. We exploit this enhancement of electromagnetic fields around such nanostructures for enhancing the sensitivity of infrared spectroscopy in two configurations: in far-field Fourier-Transform-Infrared spectroscopy (FTIR) and in spatially resolved near-field spectroscopy with a scattering-type Scanning Near-field Optical Microscope (s-SNOM).

Infrared vibrational spectroscopy is sensitive to characteristic molecule absorption bands, yielding a “fingerprint” spectrum of the molecules involved. In order to exploit the local field enhancement of optical antennas, the antenna resonance has to be tuned to the vibrational absorption band of interest. We fabricated IR antennas of triangular shape using nanosphere lithography (NSL). Spherical particles with diameters of a few micrometers served as shadowing masks during the evaporation of a thin gold film. After removal of the spheres, arrays of triangular shaped IR antennas of a well-defined size are available for further investigation. For the characterization of these structures we use diffraction-limited FTIR microscopy. Our specially equipped FTIR microscope (BRUKER Hyperion) enables us to measure reflection and transmission spectra from very small areas, e.g. $20 \mu\text{m} \times 20 \mu\text{m}$. Thus we are able to determine the resonance wavelengths of the antennas while averaging only over <100 nanostructures, reducing the errors associated with slight fabrication deviations. We can tailor the resonance wavelength of the antennas by changing the length of the antenna structure, the refractive index of the substrate below the gold triangles and the gold layer thickness. Overall, we can cover the whole mid-IR spectral range with NSL-created antennas by properly choosing the fabrication parameters [1].

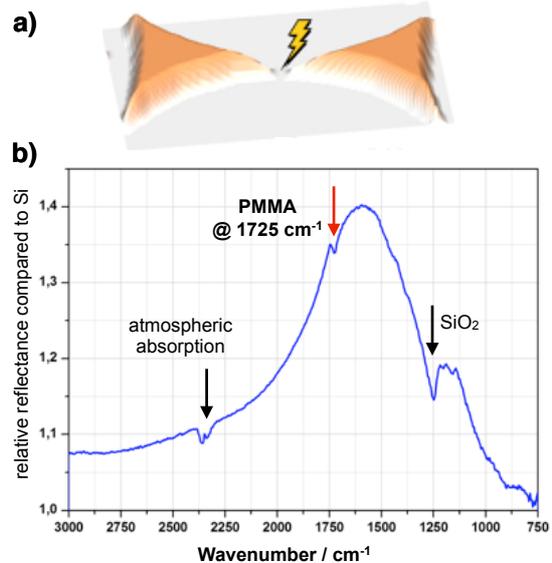


FIG. 1: a) Sketch of a gold antenna consisting of two triangles. The local electric field in the gap (indicated by yellow arrow) is expected to be strongly enhanced. b) FTIR reflection spectrum of an array of gold antennas shows a broad resonance peak at about 1600 cm^{-1} . The vibrational absorption band of a thin layer of PMMA covering the antennas is also visible in the spectrum at 1725 cm^{-1} (red arrow), proving the enhancement. Other peaks (black arrows) arise from atmospheric absorption and the (also enhanced) native SiO_2 layer on top of the silicon substrate.

In order to use these IR antennas for surface enhanced infrared absorption (SEIRA), we prepared a 40 nm thin layer of a polymer on top of the IR antennas by spin-coating. The polymer we used was polymetamethylacrylat (PMMA) and has a characteristic IR absorption band at a frequency of 1725 cm^{-1} . With the aid of the resonant enhancement by the IR antennas, the absorption band of PMMA is clearly visible (Fig 1b). With a similar integration time, the absorption signal of the PMMA on Silicon would be barely visible in the IR spectra (not shown). We observe an averaged enhancement of about 10 times. The local field enhancement however, e.g. at the tips of the IR antennas is expected to be even higher. Estimated enhancement factors of more than 4 orders of magnitude for linear antennas have been reported [2]. These factors might even be improved by an order of magnitude when employing two nanostructures separated by a small gap. Such a configuration is expected to exhibit an even higher local field enhancement due to coupling of the two neighboring structures.

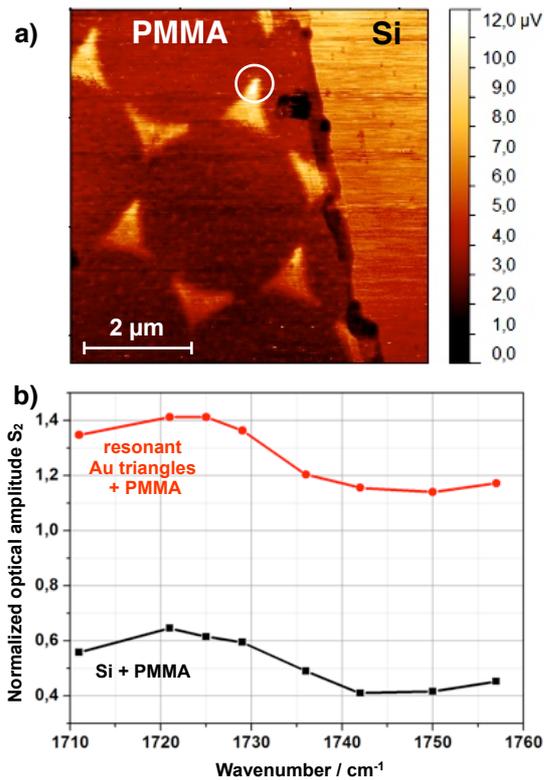


FIG. 2: a) Infrared s-SNOM image of resonant gold antennas (triangular shapes) covered with PMMA. The infrared amplitude is enhanced on the gold island compared to the bare PMMA on Si, especially on the tips of the islands, (e.g. marked with a with circle) indicating a resonant enhancement. b) Infrared s-SNOM spectra of the 40 nm thin PMMA film taken on Silicon (black) and on the bright spot of the gold triangles (red curve). The amplitude signal is enhanced by more than two times on the gold triangle.

In order to acquire information on the local field enhancement we employ high-resolution scattering-type scanning near-field optical microscopy (s-SNOM). In s-SNOM, a sharp probing tip is illuminated with infrared laser light. The electric field at the tip apex is strongly enhanced within an area of about the tips radius, which is usually in the order of 20-30 nm. The localized field interacts with the sample and allows for high-resolution probing of the samples optical properties. The spatial resolution is only limited by the tips radius of curvature and is independent of the illumination wavelength [3] Therefore, material specific imaging and chemical characterization at nanoscale resolution become possible when using infrared light for illumination. We use our infrared s-SNOM with a CO-laser as tunable mid-IR light source and illuminate the tip while scanning the sample. The backscattered light by the tip is detected interferometrically, and a demodulation procedure

enables to suppress the background light scattered by other parts of the sample.

Fig 2a shows an infrared s-SNOM image of gold triangles covered with PMMA. The infrared amplitude on PMMA is higher on gold compared to the amplitude on PMMA on the silicon surface, which is due to a substrate enhancement effect discovered already earlier [4]. Additionally, at the upper right tips of three triangles, a higher infrared signal can be observed. This is a signature of resonantly enhanced near-field spectroscopy. We evaluated the spectral response by tuning our CO-laser over the PMMA vibrational band at 1725 cm^{-1} and compared the spectra of PMMA on silicon with those obtained on the tip of the gold triangle (Fig 2b). In both spectra the vibrational absorption band is observable, and the signals on the gold triangles are enhanced more than two-fold. This is remarkable, even though we are disturbing the near-fields of the IR antenna with our metallic probing tip.

In order to minimize the disturbance of the probing tip, we plan the use of dielectric tips as well as polarization-sensitive measurements. We also envision to further increase the local field enhancement by creating structures with small gap sizes. This might allow to unambiguously measure - and not estimate- the local absorption enhancement of different kinds of IR antennas.

In summary, we have shown that infrared antennas can be used to enhance the sensitivity of vibrational spectroscopy with in conventional far-field FTIR measurements as well as in spatially resolved near-field spectroscopy (s-SNOM). One limitation of s-SNOM has been the restricted spectral range of operation due to the lack of powerful, tuneable IR laser sources. Our shown sensitivity enhancement together with the development of new broadband mid-IR laser sources at the Fraunhofer Institute of Laser Technology will push infrared spectroscopy to the level of single nanostructures, such as nanowires and particles and thus will open up exciting new possibilities for the characterization of functional nanocomposites.

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[4] J. Aizpurua, T. Taubner, F.J. Garcia de Abajo, M. Brehm, R. Hillenbrand: "Substrate-enhanced infrared near-field spectroscopy." *Optics Express* 16, 1529 (2008).