Broadband coherent hyperspectral near-field imaging of plasmonic nanostructures

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Abstract: We develop a coherent hyperspectral near-field microscope using a combined nano-Fourier Transform Infra-Red (FTIR) spectroscope and a scattering Scanning Near-field Optical Microscope (s-SNOM) illuminated by an ultra-broadband few-cycle femtosecond source, spanning a spectrum from 660 to 1050 nm. Using this spatio-spectral approach, we resolve hyperspectral near-field response of a single plasmonic nano-antennas over 450 nm bandwidth with a spatial resolution of 40 nm and a spectral resolution of 50 cm\(^{-1}\). In particular, we identify the electric near-field spatial distribution of the dipole resonant mode of various nano-antennas and observe, in accordance with previous theoretical reports, that those are spectrally red-shifted from their far-field response. Moreover, we are able to spectrally and spatially differentiate the near-field distribution of the dipole and quadrupole modes at the single nanoparticle level. Being coherent and short-pulsed, our technique opens the path for optical ultrafast characterization and control of light-matter interaction at the nanoscale.

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1. Introduction

In recent years, optical metamaterials have witnessed exponential interest and research activities stemming from the ability to design at will their optical response. The fabrication of sub-wavelength nano-structures and composite materials introduces new regimes of light-matter interaction, lead to novel frontiers in optics and electromagnetism such as optical magnetism [1], negative and zero refractive media [2–4], sensing [5–9], and nonlinear optics [10,11]. Since the plasmonic phenomena can be considered as effective medium effect [1,4], it is commonly spectrally characterized with an incoherent source and over large field of view. However, the optical response of these metamaterials nonetheless draws on the light interaction at the nanoscale with the constituent nanostructures, therefore inaccessible by far-field characterization means due to the diffraction limit.

Here, we introduce a visible-near infrared (VIS-NIR) nano-Fourier Transform Infrared (FTIR) method that allows to precisely characterize the hyperspectral near-field response at the single particle level and to unveil a much richer and complex picture of its optical behavior than possibly accessible with existing incoherent far-field techniques.

Our approach is based on a nano-FTIR [12–14] spectroscope combined with a scattering-type scanning near-field microscope (s-SNOM) (NeaSpec), and further enabled by the recent development of a few cycle octave-spanning femtosecond Ti:Sapphire laser (LQ-Venteon oscillator) (illustrated in Fig. 1(a)). The laser source delivers a stretched ultrabroadband spectrum, spanning 660-1050 nm while assuring a constant spectral dispersion over the full bandwidth. In our setup, the ultra broadband pulse is split by a beam splitter, where one pulse is focused by a parabolic mirror on an Atomic Force Microscope (AFM) tip, while another pulse is sent to a reference arm in a Michelson interferometer arrangement (Fig. 1(a)). The AFM tip interacts with the sample’s electric near-field and scatters it to the far-field. At each tip’s location, the reference mirror is swept across 100 \(\mu\)m and the interference between the
extracted near-field signal and the reference is recorded to generate an interferogram therefore allowing spectral characterization of the sample’s optical response at the tip’s location with a 30 nm spatial resolution and 50 cm$^{-1}$ spectral resolution, where the spectral resolution is determined as the inverse of the interferogram’s length.

Fig. 1. Broadband VIS-NIR nano-FTIR characterization of a plasmonic nano-antenna. (a) Schematic of scattering-Scanning Near Field Microscope tip positioned over nanostructures. The nano-antennas are spaced 500 nm apart from each other. Det: detector, PB: Parabolic Mirror. (b) AFM image of a gold nanoparticle on ITO covered glass. The nanoparticle’s dimensions are 140 × 60 × 40 nm$^3$. Scale bar is 40 nm. (c) Near-field signal of the nanoparticle due to excitation with 660-1050 nm pulse. The double-arrow indicates the polarization of the exciting pulse. The image was acquired with white-light imaging, exhibiting the collective spectral response of the near-field. (d) Near-field spectra taken at two positions, a and b. Point a, shows an enhanced scattered optical signal at 726 ± 10 nm (left y-axis). Point b does not show any spectral feature, as expected. The far-field transmission spectrum, which exhibits a resonance at 702 ± 4 nm, can be seen at red (right y-axis). Spectra were normalized relatively to the background.

2. Experimental measurements

In order to demonstrate the unique capabilities of our approach, we fabricate, using lift-off technique, an array of 30 × 30 µm$^2$ of gold nano-antennas on a SiO$_2$ substrate with an ITO adhesion layer of 30 nm. The AFM of a single nanoparticle can be seen at Fig. 1(b). We further measure the far field spectral response averaged over a 20 µm illumination spot covering hundreds of nano-antennas in a traditional FTIR spectroscopy setup and observe that the array under study has a collective absorption peak at 702 ± 4 nm at normal incidence (Fig. 1(d), red curve), for light polarized along the major axis of the nano-antennas. We then measured the response of this array in our VIS-NIR nano-FTIR setup described above. In our current measurement we have used a sharp Au-coated AFM tip (µMasch OPUS 160-AC-GG) to scatter the electric near-field to the far-field. The near-field signal of a single nano-antenna acquired through white-light imaging (without the nano-FTIR reference arm scan) is presented in Fig. 1(c). As expected for the dipole pattern, large enhancement of the near-field signal is observed on both sides of the nano-antenna, as well as a zero-intensity line at the center of the nano-antenna. We note that although previous works have shown [15] that the near-field interaction between the tip and plasmonic structures significantly changes the near-field distribution measured in the s-SNOM. These effects are, however, highly dependent on the size of the probing tip, amount and type of coating as well as the plasmonic particle’s size and resonating wavelength, explaining the lack of noticeable effect in our measurements. The tip was then positioned at the nano-antenna’s edge (point a, Fig. 1(c)) and the spectral response was acquired by scanning the nano-FTIR reference arm, extracting the full spectrum of the near-field signal, as can be seen in Fig. 1(d) after normalization with respect to the background. While the near-field signal peaks at 726 ± 10 nm, the far-field measurement shows a resonance in 702 nm. We therefore directly observe a red shift between the
resonances in the near-field and the far-field as large as $20 \pm 10$ nm, in agreement with previous theoretical report, where the red-shift in the near-field is attributed to the difference between the time-averaged absorbed power and the time-averaged kinetic energy [16]. Based on these reports, the resonance frequency in the near-field, $\omega_{0}^{NF}$, is related to the far-field resonance frequency, $\omega_{0}^{FF}$, via the following expression:

$$\omega_{0}^{NF} = \omega_{0}^{FF} \sqrt{1 - \frac{1}{2Q^2}}$$

where $Q$ is the Q-factor of the nano-antenna (resonant frequency divided by the damping constant). We thus estimate the Q-factor of the nano-antenna in this measurement to be $Q \sim 3$.

It is worth mentioning that previous experimental measurements of this resonance red-shift [17] have been shown, however those were carried out with mid-IR CW source, therefore requiring measuring many different nano-particles in the near-field at once. Our setup, on the other hand, allows us to retrieve the complete spectral response of a single nano-antenna in the near-field. Furthermore, we observe a reduced width of the nano-antenna’s resonance in the near-field compared to the far-field (Fig. 1(d)). This originates in the collective response of hundreds of nano-antennas, each having a slightly different geometry, measured in the far-field and therefore resulting in an effective broadening of the measured resonance, in accordance with the nano-antennas shape variation distribution.

![Image](https://example.com/image.png)

**Fig. 2.** Spatio-spectral near-field mapping of plasmonic nanostructures. (a) SEM image of three different gold nano-antennas. Nano-antenna length, from left to right is 130nm, 150nm and 170nm. Scale bar is 120 nm. (b) Two-dimensional, $2 \times 0.2 \mu m^2$, nano-FTIR scan of the three nano-antennas. Images at different wavelengths were then constructed. A clear resonance red-shift is observed due to the lengthening of the nano-antenna. (Visualization 1) (c) Images at three selected wavelengths, in each a different nano-antenna is seen on resonance. White scale bar is 200 nm.

To further demonstrate the spectro-spatial resolution capability of our method, we have designed and fabricated an array where the length of the nano-antennas grows gradually across the array (Fig. 2(a)). We design the length’s gradient such that the nano-antennas’ resonances span the VIS-NIR spectral region. Moreover, since the antennas are only 300 nm apart, below the diffraction limit in the range of interest, each antenna cannot be addressed individually using far-field techniques. As we show in Fig. 2(b) and in Visualization 1, we are not only able to resolve with a resolution of 40 nm each nano-antenna and its own spectral resonance, but we also collect hyperspectral data set that allows the visualization of the spatial and spectral distribution of the field enhancement over a series of nano-antennas packed beyond the diffraction limit. We note that due to the spatial resolution of the scan, which was 40 nm, we could not resolve exactly the dipole pattern of each nano-antenna. The long acquisition time (over an hour) results in damage to the scanning tip, thus reducing its spatial resolution as well as its gold coating, which reduces its effective scattering.
Finally, as the light in the s-SNOM impinges the sample at 45° incidence angle, higher resonant modes besides the fundamental dipole mode are accessible. We experimentally demonstrate this effect by scanning first a long nano-antenna with a CW illumination (Toptica DLC CTL 1550) at 1580 nm (Fig. 3(a), right). Then, by performing a hyper spectral scan across the same nano-antenna (Figs. 3(c)–3(d)) with our ultra broadband nano-FTIR setup, we have collected the response at different wavelengths. We observe that the nano-antenna with a fundamental dipole resonance at 1580 nm shows an enhanced optical signal at a wavelength of 890 nm that exhibits a quadrupole-like near-field distribution. We show in Fig. 3(c) the experimental results, amplitude and phase, as well as the corresponding Numerical FDTD simulation. Interestingly, when examining the optical phase of the signal, we see a stark difference between the expected quadrupole phase, and the experimentally observed phase in the s-SNOM. We attribute this difference to the sample-tip interaction, which, although not impacting significantly the amplitude map, appears to have a significant modulation on the spatial phase of the electric field. Figure 3(d) shows the amplitude of the nearfield for the wavelengths in the fs pulse, revealing that this mode exists only around 890 nm, in reasonably good agreement with the FDTD simulation (see Appendix A, Fig. 4).

3. Summary

In conclusion, we have introduced a unique ultra broadband VIS-NIR nano-FTIR, allowing the observation of hyperspectral near-field response with 40 nm spatial resolution at the single nano-particle level, revealing at once the spatial near-field distribution of the first and second modes of nanoparticles as a function of wavelength.

Our method can be readily extended to multi-octave bandwidths and is capable to manipulate both linear and nonlinear optical responses in various nanostructures and other condensed matter systems. Moreover, being coherent in nature, our method supports pulse shaping capabilities opening up the way to the exploration of ultrafast photo-induced hot carrier dynamics [18,19], electrons evolution toward equilibrium occurring at both
nanometric and ultra-short time scale in plasmonic nanostructures [20], 2D materials [21] and in other condensed matter compounds. This will find increasing importance in ultrafast sensing, nonlinear spectroscopy, and high speed nanophotonic devices [22–24].

Appendix A: Hyperspectral image (Amplitude and phase) - Experiment versus simulation

Fig. 4. Experimental and simulated hyper-spectral near-field response of an elongated nano-antenna. (a) Experimental amplitude (a.u). (b) Experimental phase. (c) Simulated amplitude. (d) Simulated phase.

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