

Nonlinear Plasmonic Sensing

Martin Mesch,* Bernd Metzger, Mario Hentschel, and Harald Giessen

4th Physics Institute and Research Center SCoPE, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

ABSTRACT: We introduce the concept of nonlinear plasmonic sensing, relying on third harmonic generation from simple plasmonic nanoantennas. Because of the nonlinear conversion process we observe a larger sensitivity to a local change in the refractive index as compared to the commonly used linear localized surface plasmon resonance sensing. Refractive index changes as small as 10^{-3} can be detected. In order to determine the spectral position of highest sensitivity, we perform linear and third harmonic spectroscopy on plasmonic nanoantenna arrays, which are the fundamental building blocks of our sensor. Furthermore, simultaneous detection of both methods,



providing further insight into the working principle of our sensor. While the signal-to-noise ratio is comparable, nonlinear sensing gives about seven times higher relative signal changes.

KEYWORDS: Nanooptics, plasmonics, nonlinear optics, refractive index sensing

n recent years, nonlinear effects and sensing have both been active fields in the area of plasmonics and nanooptics. While research on nonlinear plasmonics is mainly focused on the fundamental understanding of the underlying microscopic processes and how to enhance the generation of higher harmonic light,¹⁻⁹ the concept of linear plasmonic sensing already moves toward applications.^{10,11} Consequently, experiments deal with application-related topics such as large area fabrication,^{12–14} efficient analyte delivery,^{15,16} optimization of the structures with respect to sensitivity,^{17–19} and different functionalization methods for specific analytes.²⁰⁻²⁶ In plasmonic refractive index, sensing narrow line width and hence steep slopes are desirable to track even small changes. Because plasmonic resonances are usually rather broad due to radiative and ohmic losses, this is a pertinent point for improvement. An already exploited possibility is to employ dark or subradiant modes, as demonstrated with various types of Fano resonances and the plasmonic analog of electromagnetically induced transparency.^{27–29} However, experiments in nonlinear plasmonics show that the third harmonic (TH) spectrum of a plasmonic antenna is also spectrally narrower than the linear plasmon resonance. The narrowing in this case is caused by the third-order dependence of the signal on the incident light intensity. These findings suggest that a nonlinear plasmon sensor exhibits a higher sensitivity, which shall be explored in the following.

In general, plasmonic sensors can be used in different ways: First, they can be used as refractive index sensors for bulk surroundings. For example, a liquid surrounds the plasmonic nanoantenna and changes its index. This will shift the plasmonic resonance of the antenna. Second, the refractive index of the antenna itself could change, for example, when filling a palladium nanoantenna with hydrogen, causing formation of PdH, which has a different refractive index than Pd. This also will lead to a shift of the antenna resonance. Third, on the surface of the plasmonic antenna, a layer of molecules could be attached that can act as a molecular detector for binding-specific target molecules. When such binding-specific molecular recognition happens, also the refractive index of the surrounding medium changes, as the electric field enhancement is highest in the first few nanometers around the antenna.³⁰

In the linear sensing configuration, light at a frequency ω is routed through the analyte-covered nanoantennas and the transmitted or absorbed intensity at the same frequency is measured (Figure 1a). A change in the refractive index of the analyte Δn causes a resonance shift $\Delta \omega$, which directly leads to the detected intensity difference ΔT at frequency ω . Alternately, the shift $\Delta \omega$ of the resonance itself can be tracked but this requires recording the entire spectrum. The nonlinear configuration introduced here relies on the same fundamental principle but probes the resonance shift through generated light intensity at the third harmonic frequency 3ω (Figure 1b). As this light is created through a nonlinear optical process, its intensity crucially depends on the incident intensity on the nanoantennas at the fundamental frequency.³¹ Consequently, the shape of the linear absorbance spectrum is even more pronounced for the third harmonic intensity spectrum and the detectable relative intensity difference $\Delta I/I$ should be larger.

To make a more quantitative prediction of what to expect, we model our system by an anharmonic oscillator. Despite its simplicity, this model has already proven its accuracy when

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Figure 1. Principle of linear and nonlinear plasmonic sensing. A refractive index difference Δn in the environment of plasmonic nanostructures causes a shift of their resonance frequency. (a) In the linear configuration, the transmittance difference ΔT upon excitation at a given frequency ω is tracked as the sensor signal. (b) In nonlinear sensing, the plasmonic resonance is driven at frequency ω and the resonantly enhanced third harmonic at frequency 3ω serves as the sensor signal. Because of the narrowing of the TH resonance caused by the nonlinear process, a larger signal ΔI can be expected.

applied to third harmonic spectra of plasmonic nanoantennas.³²⁻³⁴ The plasmon is treated as a classical harmonic oscillator with a small third-order perturbation. Solving the differential equation of the system by means of perturbation theory yields an expression for the linear absorbance spectrum A and the emitted third harmonic intensity I

$$A(\omega) = A_0 \frac{\gamma \omega^2}{(\omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega^2}$$
(1)

$$I(\omega) = I_0 \frac{\omega^2}{((\omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega^2)^3}$$
(2)

Here, γ denotes the damping parameter and ω_0 is the resonance frequency of the unperturbed system. Assuming that scattering and absorbance exhibit the same resonant behavior and given the fact that the absolute amplitutde acts only as a scaling factor in the model, the absorbance spectrum A is approximated as 1 - T with T denoting transmittance. Hence, fitting eq 1 to experimentally obtained linear 1 - Tspectra (Figure 2a, solid lines) for pure water (blue) and 8.5 M ethanol solution (orange) surrounding the nanoantennas, we can determine γ and ω_0 . Subsequently, the generated third harmonic light intensity (dashed lines) can be calculated for the different analyte solutions. As expected, both the linear and nonlinear spectra undergo a spectral shift with a considerable line width narrowing for the TH intensity spectrum as compared to the linear absorbance spectrum. Our sensor signals are then given as

$$s_1 = \frac{\Delta T}{T_1} = \frac{T_2}{T_1} - 1 \text{ and } s_{nl} = \frac{\Delta I}{I_1} = \frac{I_2}{I_1} - 1$$
 (3)

with $\Delta T = T_2 - T_1$ and $\Delta I = I_2 - I_1$ for the linear and nonlinear sensor signals, respectively (see Figure 2b). The sensing signal is strongly enhanced in the nonlinear case, as it changes up to



Figure 2. (a) Modeled 1 - T and third harmonic spectra for pure water (blue) and 8.5 M ethanol solution (orange) in the environment of plasmonic nanoantennas. (b) Ratios of the modeled 1 - T and TH spectra, both on the same *y*-scale, demonstrating that the relative signal change is strongly enhanced in the nonlinear case.

49%, while the linear signal only exhibits a maximum change of 8%.

As an added benefit to the line width narrowing, we observe a larger amplitude of the shifted TH intensity spectrum (see inset of Figure 2a). While the amplitude at the central wavelength, given as $A(\omega_0) \propto 1/\gamma$ for the linear case, is independent of ω_0 , the TH signal at ω_0 scales as $I(\omega_0) \propto 1/(\gamma^6 \omega_0^4)$, showing a strong dependence on ω_0 . In the following, we will study the linear and nonlinear response of our system experimentally.

In our TH spectroscopy setup, laser pulses are focused on 100 \times 100 μ m² arrays of dipole nanoantennas, polarized parallel to the long antenna axis. Gold nanoantennas are fabricated by standard electron beam lithography. A sapphire substrate is used to ensure good thermal conductivity and suppress signal drifts through heating effects when conducting experiments with high pulse powers and several hours duration.³⁵ The sample is mounted in a microfluidic cell with a 70 μ m thick liquid channel. Aqueous analyte solutions can be guided to the nanoantennas by simply connecting the inlet tubing to a reservoir about 20 cm above the cell and placing the outlet to a drain below the cell level. Behind the sample, a grating spectrometer with a Peltier-cooled 2D CCD chip is used to detect the generated third harmonic light. Fundamental and second harmonic light is removed by Schott KG5 and UG11 filters. For linear transmission measurements, a white light source can be coupled into the beam path.

To perform TH spectroscopy, we shape 30 fs laser pulses with a Gaussian wavelength distribution and peak wavelengths between 910 and 1120 nm in 15 nm steps with an average power of 15 mW.³⁶ For every step, we successively record TH intensities for pure water and 8.5 M aqueous ethanol solution. The two analyte solutions have a refractive index difference of



Figure 3. Measured 1 - T (solid lines) and third harmonic (connected dots) spectra for water (index W) and 8.5 M aqueous ethanol solution (index E), corresponding to $\Delta n \approx 1.5 \times 10^{-2}$ (a–c). Three plasmonic nanoantenna arrays with different antenna length, depicted in the left column, were investigated. The ratios of the linear and nonlinear spectra, respectively, exhibit the expected dispersive shape with an extremum on both sides of the resonance, and clearly indicate a much higher relative intensity change for the nonlinear signal (d–f) and are in good agreement with the model.

 $\Delta n \approx 1.5 \times 10^{-2}$. Deionized and filtered water, devoid of biological impurities, was used throughout the experiment. Integration time of the TH signals varies between 10 and 30 s, depending on signal strength. The different integration times and background effects are accounted for by appropriate normalization. Finally, the TH signal is normalized to the signal generated by the bare substrate (as measured through the cell) and spectrally integrated to deliver a scalar value for the intensity.

In order to map the entire resonant behavior, which exceeds the available tuning range of our laser, we investigated three nanoantenna arrays with varying parameters. All antennas are fabricated with a nominal width of w = 60 nm and height of h = 40 nm but differ in length. Scanning electron micrographs in Figure 3 (left column) depict the respective antennas with lengths of l = 150, 165, and 180 nm. Linear and third harmonic spectra with increasing resonance wavelength are shown in Figure 3a-c for both analyte solutions and are evaluated by fitting eqs 1 and 2 to the respective measurement data. The linear resonances exhibit spectral shifts between 5.6 and 7.1 nm. The impression of a broadened TH spectrum for the nanoantennas covered with ethanol solution (cf. Figure 3b) is not confirmed by the fit and has its origin in the combination of spectral shift and intensity change. Furthermore, the data point at 910 nm in Figure 3c,f had to be omitted as the laser system did not allow for pulses with shape and power comparable to the previous measurements at this edge of the tuning range.

Despite the lower absolute TH intensity for the shortest antennas, all their respective ratios exhibit the expected dispersive shape centered on the resonance and clearly indicate a much higher relative signal change for the nonlinear signal (Figure 3d-f). All trends agree nicely with the modeled behavior displayed in Figure 2. Variations in absolute signal levels and deviations from the modeled behavior are well within the expected uncertainties in nonlinear spectroscopy measurements and can be attributed to tolerances in fabrication of the nanoantennas and measurements. Additionally, in a first approximation the TH sensitivity does not depend on the excitation power. Even though the incident intensity certainly has a strong influence on the absolute TH intensity, the sensor signal, as a differential signal, is not affected. In order to further investigate the behavior, we choose the spectral position denoted by the vertical dashed line in Figure 3d to directly compare linear and nonlinear sensing in the following. This wavelength is close to the maximum sensitivity for both methods and the selected antenna array exhibits the maximum nonlinear sensitivity $\Delta I/I$ of the presented structures.

For a sound comparison, it is most favorable to detect linear and nonlinear signals simultaneously. Therefore, we modify our setup and replace the spectrometer by two separate detectors. Light at the fundamental and third harmonic wavelengths is split spatially by a prism sequence and routed into a silicon photodiode and a photomultiplier tube (PMT), respectively. The two detector signals are fed into identical lock-in amplifiers to ensure equal signal treatment. The associated light chopper is inserted in front of the focusing optics of the beam incident to the sample. Again, Schott UG11 filters are used to protect the PMT from stray light.

The measurement is carried out on the 150 nm antenna array at 970 nm incident wavelength (as denoted in Figure 3d) with an average on sample power of 5 mW, focused onto a diameter of 50 μ m. Six aqueous ethanol analyte solutions are prepared by a dilution series with concentrations corresponding to $\Delta n \approx (150, 60, 30, 15, 6, 3) \times 10^{-4}$ with respect to the refractive index of pure water. Decreasing concentrations of analyte solutions are, alternately with pure water, filled into the sensor cell in a continuous measurement. Data points are recorded every 200 ms and are subsequently averaged by a percentile filter with a span of 60 s.

The resulting time traces are plotted in Figure 4a. The nonlinear signal shows a maximum increase as high as 70% for



Figure 4. Time traces of linear and nonlinear signals for decreasing concentrations of ethanol in water (W). Both signals were recorded simultaneously on 150 nm length antennas and at a wavelength of 970 nm, corresponding to roughly the maximum of both sensitivity curves. (a) The nonlinear signal provides a maximum increase as high as 70% for concentrated ethanol solution, whereas the linear signal decreases by approximately 10%. (b) Normalized to an interval of 0 to 1, it becomes apparent that the signal-to-noise ratio is almost equal for linear and nonlinear signals. Therefore, both methods allow for detection of refractive index changes on the order of $\Delta n \approx 10^{-3}$.

concentrated ethanol solution, whereas the linear signal decreases by approximately 10% for the same concentration. Those results are consistent with the values from the previous spectroscopy measurements (at the spectral position indicated by the vertical dashed line in Figure 3d). Although high signals are desirable for a sensor, equally important values are signal-to-

noise ratio and, closely related, the limit of detection. In order to compare those quantities for both methods, we invert the linear signal and normalize both signals to an interval from 0 to 1 (Figure 4b). In this representation, it becomes apparent that the signal-to-noise ratio is almost equal for both methods, leading to an estimated detection limit of $\Delta n \approx 10^{-3}$.

In summary, we introduced nonlinear plasmonic sensing to enhance the sensitivity of localized surface plasmon resonance sensors. The strong dependence on the local electric fields of the nanoantennas in the process of third harmonic generation gives rise to a distinct increase of the sensor signal. The spectral behavior of the nonlinear signal obtained by third harmonic spectroscopy could be described by an anharmonic oscillator model. In direct comparison, it turns out that both methods reproduce the refractive index changes equally well and no distortion occurs due to the nonlinear process. Future investigations could include nonlinear sensors that do not just rely on a shift of the resonance frequency but on a change of the damping parameter γ such as, for example, in palladiumbased plasmonic hydrogen sensors.^{37,38} The benefit of this method lies in the fact that damping contributes drastically to the generated third harmonic intensity. Therefore, even higher enhancement might be achievable. Other sensing schemes that rely on alternative nonlinear wavemixing processes are also available, such as SHG, 39-41 SFG, DFG, or FWM. Particularly interesting could be the combination of anisotropic liquids with resonant nanoantennas, which could break inversion symmetry and enhance especially $\chi^{(2)}$ processes. This will also become relevant when going from bulk refractive index sensing toward surface-functionalized sensing, where individual small molecules or thin molecular layers, directly on the surface in the region of highest field enhancement, generate the nonlinear optical effects. Especially when considering second harmonic generation, the symmetry of the molecules and their specific orientation might result in additional nonlinear optical signals.42

AUTHOR INFORMATION

Corresponding Author

*E-mail: m.mesch@pi4.uni-stuttgart.de.

Author Contributions

M.M. and B.M. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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