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Low-Power Photothermal Probing of Single Plasmonic Nanostructures with Nanomechanical String Resonators

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Supporting Information

ABSTRACT: We demonstrate the direct photothermal probing and mapping of single plasmonic nanostructures via the temperature-induced detuning of nanomechanical string resonators. Single Au nanoslits and nanorods are illuminated with a partially polarized focused laser beam (λ = 633 nm) with irradiances in the range of 0.26−38 μW/μm². Photothermal heating maps with a resolution of ∼375 nm are obtained by scanning the laser over the nanostructures. Based on the string sensitivities, absorption efficiencies of 2.3 ± 0.3 and 1.1 ± 0.7 are extracted for a single nanoslit (53 nm × 1 μm) and nanorod (75 nm × 185 nm). Our results show that nanomechanical resonators are a unique and robust analysis tool for the low-power investigation of thermoplasmonic effects in plasmonic hot spots.

KEYWORDS: Plasmonic hot spots, thermoplasmonics, nanomechanical resonators, optical heating, photothermal mapping

Subwavelength noble metal structures (nanoparticles or nanovoids) support localized surface plasmon (LSP) resonances that usually occur in the visible and near-infrared spectral region. The incident light can couple to LSP modes producing extremely large field enhancements, so-called hot spots. These strong field confinements are prominently utilized e.g. in surface-enhanced Raman scattering (SERS) spectroscopy,1−4 in plasmonic solar cells,5−9 or as nano heat sources with a wide range of potential applications.10−12 When a plasmonic nanostructure is illuminated with an incident light, part of it is scattered into the surrounding medium, while the other part is absorbed and dissipated as heat. Interestingly, optical and thermal hot spots are generally mismatched. Baffou et al. have shown experimentally that heat is concentrated in areas where charges can freely flow, while optical hot spots usually appear at the metal interface with the greatest charge accumulation (tip effect).10 So far there have been a few attempts to investigate the photothermal heating of metal nanostructures using thermal-optical13 and thermoresistive14 techniques and an AFM tip.15 However, the desirable direct investigation of the heating mechanisms in plasmonic structures is still a challenge due to the lack of robust experimental tools.10 Herein we propose a new approach to probe and image plasmonic structures with submicrometer resolution by measuring the photothermally induced frequency detuning of highly temperature sensitive nanomechanical resonators. It has been shown that plasmons can be coupled to the vibration of a nanomechanical resonator.16 We employ the high temperature sensitivity of a nanomechanical string resonator17,18 to directly probe the heating pattern produced by single Au nanoslits and nanorods illuminated by a partially polarized scanning laser beam. The experimental approach allows a sensitive heat mapping of noble metal nanostructures to study heat generation and thermal diffusion in e.g. plasmonic hot spots.

The proposed method to photothermally probe plasmonic nanostructures is schematically illustrated in Figure 1. Single Au nanoslits and nanorods were chosen as a nano heat source. The

Figure 1. Schematic depiction of the experimental setup. A nanomechanical SiN string resonator is partially coated with a Au layer. A plasmonic nanoslit or nanorod (etched with a focused ion beam) is located in the string center and probed with a low-power focused laser beam from a laser-Doppler vibrometer. The inset shows the thermal fluctuation spectrum of a 900 μm long micromechanical SiN string resonator.

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nanostructures were milled using a focused ion beam (FIB) (using a 30 kV Ga+ beam with current of 9 pA) into the Au metal coating of a nanomechanical silicon nitride (SiN) string resonator. The fabrication of the SiN string resonators is described elsewhere. The string resonance frequency corresponds to the thermal vibration of the string (see inset of Figure 1), measured in high vacuum with a laser-Doppler vibrometer (MSA-5 from Polytec). The partially polarized vibrometer’s laser beam ($\lambda = 633$ nm, full width at half-maximum $\text{FWHM} = 0.9 \, \mu\text{m}$ with $50X$ objective) is utilized to simultaneously record the string resonance frequency and excite localized and surface plasmons in individual Au nanoslots and nanorods. Minimal and maximal irradiances of $L = 0.26-8.3 \, \mu\text{W}/\mu\text{m}^2$ and $I = 1.1-38 \, \mu\text{W}/\mu\text{m}^2$ with the 20X and 50X objective, respectively, were used. Part of the incident light is absorbed by a nanostructure and dissipated into heat. The string resonator is highly temperature sensitive and can be used to monitor the photothermal heating produced by the nano heat source on the string via the resonance frequency detuning.

In vacuum and for low photothermal heating, the absorbed energy from a nanostructure is transferred off a string mainly by thermal conduction. In this case, the relative frequency change $\Delta f$ per absorbed power $P$ in the center of a string resonator is given by

$$\frac{\Delta f}{P} = \frac{L}{16\pi h} \frac{\alpha E}{k}$$

(1)

with the string length $L$, thickness $h$, width $w$, thermal expansion coefficient $\alpha$, Young’s modulus $E$, tensile prestress $\sigma$, and thermal conductivity $k$. From eq 1 it can be seen that the sensitivity is highest for long and slender strings with a low thermal conductivity. In order to improve the sensitivity, the highly conductive Au film was removed by FIB milling at the anchors of some strings.

The absolute value of the electric field around a 2-dimensional (infinitely long) Au nanoslot was simulated using the finite element method (FEM). Figure 2a shows the $|E|$ map in a string cross section for s-polarized (perpendicular) and p-polarized (parallel) incident light with respect to the nanoslot orientation. In the s-polarized case the incoming field is enhanced around the slit due to the localized nature of the plasmonic excitation. Additionally, a surface plasmon polariton (SPP) is launched at the metal–insulator interface. In the p-polarized mode, the LSP generation is minimized. The resistive loss and thus the heating in the metal of a string is roughly 5 times larger for s-polarization compared to p-polarization. The polarization-dependent photoinduced heating of the string resonator is tested using three identical nanoslots with different orientations as shown in Figure 2b. Photothermal maps of a vertical and horizontal plasmonic slit with a partially horizontally polarized laser beam (using 50X objective) with an irradiance of $I = 11 \, \mu\text{W}/\mu\text{m}^2$. (d) Schematic calculation of the heating ratio between a vertical and horizontal nanoslit. (e) Resonance frequency of the string for a scan over all three plasmonic nanoslits for two perpendicular laser orientations with $I = 25 \, \mu\text{W}/\mu\text{m}^2$.


Figure 3. (a) SEM image of nanotip in the center of a silicon-rich SiN nanostring (σ = 200 MPa, L = 550 nm, w = 1 μm, h = 220 nm, covered with 50 nm Au). (b) Measured relative resonance frequency of this nanotip as a function of laser irradiance when focused on the plasmonic nanotip and when focused beside the nanotip (using 20X objective). (c) Difference of the relative resonance frequency δf caused by the photothermal heating of the plasmonic nanotip. The right y-axis further shows the power P absorbed by the nanotip and the resulting local temperature increase ΔT. The error bars represent the standard deviation of three measurements.

(μW/μm²) can be extracted. With a sensitivity of the nanotip of δf/P = −2.51 ± 0.13%/μW (see Supporting Information), this results in an absorption cross section of P/ΔT = 0.12 ± 0.01 μm². This corresponds to an absorption efficiency of 2.3 ± 0.3 for the nanotip with a geometrical area of 0.053 μm². The local temperature in the center of the nanotip increases by ΔT/ΔI = 21.5 ± 3.2 K/μW (see Supporting Information), which results in a nanotip-induced heating per irradiated light of ΔT/μm = 2.6 ± 0.5 K/(μW/μm²). Both the absorbed power P and the local temperature increase ΔT are plotted on the right y-axis of Figure 3c.

As a comparison to the plasmonic nanotips which excite both LSPs and SPPs (see Figure 2a) we probed a plasmonic Au nanorod which only supports LSPs. Figure 4a shows the SEM image of a nanorod etched in the Au coating of a 1 μm wide nanomechanical string. The photothermal maps around the Au nanorod for s-polarization (top) and p-polarization (bottom) are shown in Figure 4b. In the s-polarized map, the distinct heating pattern of the nanorod is clearly visible whereas in the p-polarized map it is indiscernible from the background. The nanorod has an LSP resonance close to 633 nm along its short side, as can be seen from Figure 4c, whereas the absorption efficiency has a minimum along its long side. This measurements indicates the photothermal detection of a single nanorod via its LSP. From the relative frequency change δf caused by the Au nanorod, shown in Figure 4d (similar to Figure 3c), a sensitivity of δf/ΔT = −90 ± 60 ppm/(μW/μm²) can be extracted. From the string sensitivities of δf/P = −6.1 ± 0.5 ppm/nW and ΔT/ΔI = 12.7 ± 1.9 K/μW (see Supporting Information), it is possible to calculate the absorption cross-section P/ΔI = 0.015 ± 0.010 μm² and temperature increase per irradiance ΔT/ΔI = 0.19 ± 0.13 K/(μW/μm²). Both the absorbed power P and the local temperature increase ΔT are plotted on the right y-axis of Figure 4d. From the absorption cross section an absorption efficiency of 1.1 ± 0.7 can be calculated for the nanorod with a geometrical area of 0.014 μm². This corresponds well with the calculated absorption efficiency of 1.3 as depicted in Figure 4c, and it is roughly half the absorption efficiency of the nanotip. This difference can mainly be assigned to the additional SPPs launched at the nanotip which contributes strongly to the overall absorption.

The typical irradiances used in this experiment of a few μW/μm² is 1–4 orders of magnitude lower than the illuminances typically used in state-of-the-art probing of plasmonic nanostructures.11,13,14 Low irradiances are critical for studying thermal hot spots with (bio)molecules adsorbed on the metal surface to avoid photochemistry related effects or thermal decomposition of adsorbates.

In conclusion, we demonstrate the low-power photothermal probing and mapping of single plasmonic Au nanoslits and nanorods via the temperature-induced detuning of the resonance frequency of nanomechanical SiN string resonators.
The polarization-dependent heating patterns are mainly observed in the vicinity of the nanostructures that can be attributed to excited LSPs and the additional SPPs at the Au/SiN interface of the nanoslits. We produced a photothermal map with a resolution of $\sim 375$ nm by scanning the focused probing laser over the nanostructure area. Based on the string sensitivities, absorption efficiencies of 2.3 $\pm$ 0.3 and 1.1 $\pm$ 0.7 for a nanoslit (53 nm $\times$ 1 $\mu$m) and nanorod (75 nm $\times$ 185 nm), respectively, were extracted. The increased absorption of the nanoslit can be assigned to the additional excitation of LSPs. Our results show that nanomechanical resonators are a unique and robust tool for probing thermal effects in plasmonic nanostructures.

■ ASSOCIATED CONTENT

5 Supporting Information

String sensitivity calculations and nanorod dipole model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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