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Published in:
ACS Sensors

Link to article, DOI:
[10.1021/acssensors.0c00591](https://doi.org/10.1021/acssensors.0c00591)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Padmanabhan Rangacharya, V., Wu, K., Larsen, P. E., Thamdrup, L. H. E., Ilchenko, O., Hwu, E. T., Rindzevicius, T., & Boisen, A. (2020). Quantifying Optical Absorption of Single Plasmonic Nanoparticles and Nanoparticle Dimers Using Microstring Resonators. *ACS Sensors*, 5(7), 2067–2075.
<https://doi.org/10.1021/acssensors.0c00591>

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ACS Sens., **Just Accepted Manuscript** • DOI: 10.1021/acssensors.0c00591 • Publication Date (Web): 12 Jun 2020

Downloaded from pubs.acs.org on June 17, 2020

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Quantifying Optical Absorption of Single Plasmonic Nanoparticles and Nanoparticle Dimers Using Micro String Resonators

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KEYWORDS: Micromechanical string resonators, thermoplasmonics, plasmonic heating, nanoparticles, absorption cross sections

ABSTRACT: The wide and ever-increasing applications of thermoplasmonics demand the need for sensitive and reliable tools to probe optical absorptions of individual nanoparticles. However, most of the currently available techniques focus only on measuring surface temperature of nanostructures in a particular medium, and are either invasive or suffer from low sensitivity, lengthy calibration or the inability to probe single structures with nanogaps. Here, we present for the first time the use of micromechanical SiN string resonators for quantifying optical absorption cross sections of individual plasmonic nanostructures. Monomers and dimers of nanospheres, nanostars, shell-isolated nanoparticles and nanocubes are probed. A reliable data treatment method is developed to obtain the absorption cross sections as a function of responsivity across a string. The presented method exhibits an excellent sensitivity of ~89 Hz/K. This allows quantification of optical absorption cross sections of individual plasmonic structures even when their plasmon resonance wavelengths are far from that of the laser excitation wavelength. The experimentally obtained optical absorption cross sections agree well with the simulations. Influencing factors including polarization, surface morphology and nanogap size are discussed. The developed method and the obtained optical absorption profiles facilitate future development and optimization of thermoplasmonic applications.

Nanoplasmonics deals with the resonant coupling of incident photons with free electron oscillations in materials.^{1,2} The phenomenon is also known as surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR).³ Nanoplasmonic materials, mostly metal nanoparticles (NPs), can focus light beyond its diffraction limit.^{2,4} This leads to significant electromagnetic (EM) near-field enhancements and results in strong scattering and absorption of light.⁵ Particularly, the strong absorption gives rise to the generation of heat and its subsequent dissipation into the surrounding medium.⁴ Recently, nanoplasmonic heating, a.k.a. thermoplasmonics, has become a hot topic, due to its huge potential in a variety of applications, such as photothermal cancer therapy,^{6–10} photothermal drug delivery,^{11–13} photothermal imaging,^{14–16} and heat-assisted nanochemistry.¹⁷ In 2019, more than 300 journal articles mentioning thermoplasmonics or plasmonic heating were published according to Web of Science Core Collection.¹⁸

To facilitate applications of thermoplasmonics, there is a need to develop reliable measurement techniques to accurately measure (i) nanoscale surface temperatures and (ii) nanoscale heat sources, i.e., absorption cross sections of individual plasmonic nanostructures. It is very challenging to achieve both. Most works focus on the former. They can be divided into two categories: near-field and far-field based techniques. Near-field methods, such as scanning thermal microscopy¹⁹ are invasive, and may damage the probed nanostructures. Far-field methods, such as thermally induced refractive index change,²⁰ surface-enhanced Raman spectroscopy (SERS),²¹ photoluminescence²² and fluorescence polarization anisotropy,²³ could suffer from lengthy and complex calibration processes, slow-read out rate, low-resolution, or poor temperature sensitivity. In particular, the technique that monitors the thermal-induced variation of the refractive index²⁰ requires optically transparent samples, a liquid environment and considerable experimental and computation efforts. The SERS-based method²¹ monitors the temperature dependent position of

the $\text{N}\equiv\text{C}$ vibration mode of phenyl isocyanide (PIC) adsorbed on a SERS substrate made of Au. Though relatively simple, it lacks general applicability, i.e., it can only be used to probe surface temperature of SERS substrates, and has only been demonstrated on an Au substrate. Furthermore, obtaining reliable, temperature-dependent SERS signals from single nanoparticles or nanoparticle dimers covered by PIC would be extremely difficult due to (i) varying PIC surface coverage and (ii) low SERS signal intensities, especially when the plasmon resonance is far from the incident laser wavelength. The reported photoluminescence-based thermal sensor²² needs to be calibrated using the theoretical extinction cross section derived by employing the electric dipole approximation. This means that the sensor cannot be used to evaluate heating produced by the EM hot spots where multipoles play an important role. The method is limited to single, ellipsoidal particles with ~ 40 nm in diameter or less. The fluorescence polarization anisotropy²³ method offers a direct measurement of the local temperature. However, the reported fluorescence polarization anisotropy maps lack resolution to image single plasmonic particles or dimers that feature nanogaps. Recently, a method based on a customized integrating sphere has been developed to measure absorption cross sections of single plasmonic nanoparticles with submicron spatial resolution.²⁴

Micro- and nanomechanical string resonators have lately received significant attention due to their extraordinarily high Q-factors that makes them ideal platforms for ultra-sensitive sensing.²⁵ Recently, the use of Ni, Al and SiN (silicon nitride) micro- and nano string resonators as ultra-sensitive temperature sensors has been explored.^{26,27} The developed temperature sensors exhibit a small thermal mass and a short response time.²⁷ In addition, local temperature probing of a single plasmonic Au nanoslit and a single Au nanorod, has been achieved on a SiN string resonator, taking advantage of the low thermal conductivity of SiN.²⁸ However, the method is not applicable to obtaining optical absorption cross section, which relates to efficiency of nanoscale heat generation and is thus a key parameter. Moreover, string resonators have not yet been employed to probe absorption cross sections of and temperatures near single plasmonic NPs and their dimers, which are extremely important for practical applications.^{1,7,9,29} The challenge mainly results from the fact that the NPs can spread across a string after sample preparation, each triggering a unique, position-dependent responsivity of the string, leading to different relative vibration frequency shifts even under identical excitation conditions.

Here, we present a first study on quantifying optical absorptions of individual plasmonic NPs and NP dimers using SiN string resonators. The probed NPs and NP dimers are composed of Au nanospheres (AuNS), shell-

isolated Au NPs,³⁰ Ag nanocubes (AgNC) and Au nanostars. A superb sensitivity of ~ 89 Hz/K is achieved. This allows quantification of optical absorption cross sections of individual plasmonic structures, even when their plasmon resonance wavelengths are far from that of the excitation. A reliable data treatment model is developed to unravel the absorption cross sections of the probed NPs as a function of string responsivity, their positions on the string, and other parameters. The experimentally probed optical absorptions are in close agreement with those calculated via FEM simulations. Influencing factors such as polarization, surface morphology and nanogap size are discussed as well. Our study facilitates the use of plasmonic NPs to accurately control temperature at the nanoscale for future practical applications.

MATERIALS AND METHODS

Fabrication of SiN Strings: SiN micromechanical string resonators (Figure 1A) were fabricated in a cleanroom. Approximately 200 nm low-stress SiN was deposited on a double-side polished $\langle 100 \rangle$ Si wafer with a thickness of 350 μm by low-pressure chemical vapor deposition (LPCVD). The string pattern was transferred to the front side SiN using conventional UV lithography and reactive ion etching (RIE). A protective layer of SiN was deposited on top of the patterned front side by a low-frequency plasma-enhanced chemical vapor deposition (PECVD) process. Using UV lithography and RIE, a window was patterned on the back side of the wafer for subsequent release of the strings through potassium hydroxide (KOH, 28%) etch conducted at 80 $^{\circ}\text{C}$. The protective PECVD SiN layer was etched away in buffered hydrofluoric acid (1:7 BHF: DI water) at room temperature. The dimensions of the strings fabricated were 760 x 50 x 0.2 μm (AuNS), 760 x 15 x 0.2 μm (shell-isolated Au NPs), 1018 x 30 x 0.2 μm (AgNC) and 900 x 50 x 0.2 μm (Au nanostars).

Deposition of NPs onto SiN Strings: As shown in Figure 1B, four types of NPs were deposited: i) AuNS of ~ 200 nm in diameter. $\lambda_{\text{LSPR}} \approx 600$ nm (Sigma Aldrich), ii) shell-isolated Au NPs, i.e., silica-shelled AuNS, of ~ 100 nm in diameter with a shell thickness of ~ 15 nm. $\lambda_{\text{LSPR}} \approx 585$ nm (Nanocomposix), iii) AgNC of ~ 100 nm in side length. $\lambda_{\text{LSPR}} \approx 565$ nm (Nanocomposix), and iv) Au nanostars (urchins) of ~ 100 nm in diameter. $\lambda_{\text{LSPR}} \approx 680$ nm (Sigma Aldrich). A simple manual deposition method was adopted. A 3 μL droplet of $\sim 5\%$ solution of NPs was pipetted onto the surface of the strings. After drying, various configurations of NP clusters were obtained, including monomers, dimers, and clusters that contained multiple NPs.

SEM Characterization: A field emission Zeiss Supra 40VP scanning electron microscope equipped with a Gemini column was used to locate and image NPs on the strings. High vacuum mode was used. The acceleration voltage was

10 kV. All samples were imaged directly without additional coating.

Photothermal Probing: The experimental setup is sketched in Figure 1C. The chip containing the strings with the deposited NPs was firmly attached on the top of an RXY stage (SmarAct GmbH). A piezoelectric actuator (Noliac A/S) was attached to the stage. This system was subsequently placed inside a vacuum chamber ($<10^{-5}$ mbar). A laser-Doppler vibrometer (LDV) (MSA-500 from Polytec GmbH) was used to measure the resonance frequency of the strings. The vibrometer was fitted with a 50X, 0.42 NA objective (SEIWA Optical, Japan). A 633 nm HeNe laser was used for both probing and reading. This laser was partially polarized with an intensity ratio of 4.2:1. For photothermal imaging, a 512 x 512 scanning grid large enough to encompass the NP(s) was employed.

Figure 1. (A) An SEM image of the SiN micromechanical string resonators. (B) Schematic of a 633 nm laser illuminating a certain area on a SiN string that contains the probed NPs. (C) Schematic describing the experimental setup. A low power laser from a laser-Doppler vibrometer is used to probe NPs on a SiN string. A chip contains 25 strings. The chip is mounted on top of an RXY-stage capable of rotational and translational movements. (D) Schematic of the basic measurement

principle, showing the corresponding detuning of resonance frequency of the SiN string in response to plasmonic heating of the NPs.

Measurement principle: Structurally, micromechanical string resonators are a special case of doubly clamped beams. Because of their high tensile stress, their flexural rigidity becomes negligible resulting in string-like behavior.^{31,32} Thus, the resonance frequency, f_0 , of a micromechanical string resonator can be obtained via:²⁷

$$f_0 = \frac{n}{2L} \sqrt{\frac{\sigma}{\rho}} \quad (1)$$

where n is the resonant mode number, L is the length of the string, σ is the tensile stress and ρ is the mass density of the string. In addition, the resonance frequency of a micromechanical resonator is a function of temperature. The localized temperature dependent resonance frequency $f(T)$ of the string is given by:

$$f(T) = \frac{n}{2L} \sqrt{\frac{\sigma - E \alpha_{str} \Delta T}{\rho}} \quad (2)$$

Here, E is the Young's Modulus of the string material, α_{str} is the thermal expansion coefficient of the string and ΔT is the change in temperature. Temperature induced changes in E , ρ and L can be neglected in this model.^{26,27} The difference in resonance frequency (Figure 1D) can be attributed to the heat generated by the the plasmonic NP(s). The relative shift in frequency δf in a string is given by:

$$\delta f = \frac{f(T) - f_0}{f_0} \quad (3)$$

Substituting equation (3) with (1) and (2), we arrive at equation (4), which calculates the change in temperature ΔT as a function of the relative frequency shift δf , which is obtained experimentally:

$$\Delta T = 2 \frac{\rho (2Lf_0)^2}{E \alpha_{str}} [1 - (\delta f + 1)^2] \quad (4)$$

Data analysis: The photothermal imaging of the NPs is performed by scanning the string surface using an LDV, shown in Figure 2A. The subsequent data analysis is illustrated in Figure 2B-H. Specifically, first, the measured resonance frequency values at each point are fitted using a quasi-Lorentzian fit (Figure 2B), as the amplitude response of the string resonator can be approximated by a quasi-Lorentzian function.³³ Then, baseline correction is performed (Figure 2C). Small sources of noise such as frequency drift over time or non-perfect angular alignment are removed by fitting a plane to the spatially distributed resonance frequency measurements.

Figure 2. (A) An LDV is used to probe the NP(s). A scanning grid is first created to encompass the NP(s). Afterwards, the resonance frequency is measured at each point on the grid. (B-H) Detailed data analysis steps. (B) The measured resonance frequency values at each point are fitted using a quasi-Lorentzian fit. (C, D) Baseline correction and outlier elimination followed by determination of the resonance frequency f_0 of the string resonator. (E) A starting point for a Gaussian fit is defined by identifying the peak in the map. (F) A photothermal image represented by the relative frequency shift δf is subsequently obtained after a 2D Gaussian fit. (G) The effects of location of NP(s) on the string are removed according to responsivity of the string. (H) Irradiance normalization is performed to estimate the fraction of laser power directed at the NP(s) contributing to the frequency shift.

Afterwards, outliers introduced by dirt or other imperfections on the string or in the optical path of the LDV laser are removed (Figure 2D). Subsequently, a starting point for a Gaussian fit is set by picking the center of the absorption peak with a diameter (Figure 2E,F). The diameter corresponds to FWHM of the 2D intensity distribution of the readout laser beam. Next, the location effect due to responsivity of the string (Figure 2G) is normalized. The responsivity ($\mathfrak{R}$) of a string resonator to a point source of power directed at its center is given by:³³

$$\mathfrak{R} = -\frac{1}{16} \frac{EL^{\alpha_{\text{str}}}}{\kappa A \sigma} f_0 \quad (5)$$

where A is the cross-sectional area of the string resonator and κ is the thermal conductivity of the string material. Modifying equation (5) suitably for the case when the point source of power (and hence, heat) is directed at any arbitrary point 'x' along a string of length L , we can compute responsivity ($\mathfrak{R}$) of the absorbed power at 'x' as:

$$\Re = -\frac{E\alpha_{str}}{8\kappa AL\left(\frac{1}{x} + \frac{1}{L-x}\right)\sqrt{\frac{\sigma}{\rho}}} \quad (0 \leq x \leq L) \quad (6)$$

Equation (6) clearly indicates that the responsivity of the string varies across the length of the string, and reaches maximum at the string center. Then, irradiance normalization is performed to estimate the fraction of laser power directed at the NP(s) contributing to the frequency shift, in accordance with the fitted laser beam intensity profile (Figure 2H). This step takes into account variations in the focus of the readout laser, which in turn change the local irradiance at the nanoscale. Finally, the experimental absorption cross sections of the probed NPs are obtained by $P_{abs}/P_{total} \cdot S$, where P_{abs} is the laser power absorbed by the NP(s), P_{total} is the excitation laser power, and S is the area of the laser spot.

FEM Simulation: 3D FEM simulations were performed using COMSOL MULTIPHYSICS version 5.4. The EM field distribution was calculated by solving the full field. A domain-backed port, located at the top of the solution domain, was used to excite the linearly polarized incident EM field. A perfectly matched layer (PML) was employed to eliminate nonphysical reflections. Scattering boundary conditions were employed on the top and bottom boundaries of the PML layer to further reduce reflection. For the side planes of the solution domain, Floquet periodicities were used. The geometry of the NPs was modelled according to SEM images. The SiN string was modelled as a substrate below the NPs. Materials were modeled by their complex refractive indexes as functions of wavelength.³⁴⁻³⁶ The structures were surrounded by vacuum. The absorption cross section, i.e., plasmonic heating, is calculated by

$$\sigma_{abs} = \frac{1}{I_0} \iiint Q dV \quad (7)$$

where I_0 is the intensity of the incident laser, and Q is the power loss density of the NP(s).

RESULTS AND DISCUSSION

We start from probing the heating of NPs on string resonators and then use the data analysis model detailed in the data analysis section to translate the heating profiles to optical absorption cross sections. Note that when probing plasmonic NPs on a string, the measured relative frequency shift δf could also be due to direct laser heating of the string, or vibrational couplings between the NPs and the string.³⁷ To clarify their contributions to the relative frequency shift, the following two experiments are first performed:

(I) The frequency shifts of a bare string, heated by a laser with powers to be used for probing the plasmonic NPs, are measured. Results are shown in Figure S1 in the supplementary. It can be seen from Figure S1 that the relative frequency shift of the string increases from ~3 to ~13 ppm when increasing laser power from 40 to 140 μ W. These frequency shifts are significantly lower than those measured on plasmonic NPs placed on strings, shown later in the paper. Specifically, the direct laser heating of the string accounts for only <3% of the total relative frequency shift. Therefore, it can be concluded that the contribution of direct laser heating of the string to the total frequency shift is negligible.

(II) Vibration frequencies of a blank quartz fragment, and of the same fragment covered by an AuNS dimer, are measured. For the latter, the probing laser is focused on the center of the dimer. Results are shown in Figure S2 in the supplementary. Figure S2 shows that the relative frequency shift is only 9.7 ppm when probing the AuNS dimer on the quartz fragment. This shift could be due to the vibrational coupling between the AuNS dimer and the quartz.³⁷ On a string, under the same experimental condition, the measured relative frequency shift is ~700 ppm (shown in the next section), which is considerably higher. Note that the coupling effect could be enhanced on a string resonator. However, a good agreement between the simulated and the experimentally obtained absorption cross sections (shown later in section 'Optical absorptions of probed NPs') suggests that the major contribution to the probed relative frequency shifts is plasmonic heating.

Probing local heating of AuNS(s): We start with a simple plasmonic system - a single AuNS. A single AuNS shown in Figure 3A (left) is irradiated by a 633 nm HeNe laser in two orthogonal polarizations, and at four different laser powers (40 μ W, 60 μ W, 106 μ W and 140 μ W) for each polarization. Note that the laser is partially polarized with an intensity ratio of 4.2:1. This also applies to all subsequent experiments in the following sections. Figure 3B shows the relative frequency shift δf and the corresponding maximum temperature increase ΔT_{max} (calculated using equation 4) versus laser power. The inset in Figure 3B shows a heatmap generated from the Gaussian fitting (Figure 2F) of the resonance frequency data obtained during probing. It can be seen from Figure 3B that both δf and ΔT_{max} vary linearly with incident laser power. This is in accordance with the linear relationship between ΔT and absorbed laser power P for small temperature changes, given by the equation³³

$$\Delta T = \frac{1}{4\kappa A} P \quad (8)$$

Ideally, for a single AuNS, the heating should be the same in both polarizations. However, Figure 3B shows a slight difference. By eliminating the effect of the partially

polarized intensity ratio (4.2:1) of the laser used in the experiment, and after normalizing irradiance to take into account only the fraction of laser power directed at the NP that leads to the frequency shift (see section ‘Data analysis’), a polarization-dependent heating ratio of 1.1 is obtained. This can be attributed to the slight asymmetric geometry of the probed single AuNS. Note that for the rest of the paper, all the experimental heating ratios are obtained using this method.

Figure 3. (A) SEM images of the probed AuNS monomer and dimer. (B, C) The relative frequency shift Δf and the corresponding maximum temperature increase $\Delta T_{\max}$ versus incident laser power under two orthogonal polarizations for (B) a single AuNS and (C) an AuNS dimer. The insets show representative photothermal images depicting the decrease in resonance frequency on the SiN strings under both polarizations. (D) Simulated EEF across the center plane of an

AuNS dimer on SiN under the two polarizations at 633 nm excitation.

Next, a more complex plasmonic system is probed – an AuNS dimer, which is important for applications such as trace molecule detection using SERS^{38,39} and photothermal plasmon-assisted cancer surgery.⁹ A single AuNS dimer shown in Figure 3A (right) is probed using the same partially polarized 633 nm HeNe laser in two orthogonally different polarizations – along and perpendicular to the dimer axis, and using four incident laser powers. Results are shown in Figure 3C. Similar to the case of the single AuNS, a clear linear relationship between laser power and the temperature induced relative frequency shift is observed. In addition, a difference in the heating efficiency for each polarization direction is observed. Particularly, the relative frequency shift and consequently the temperature increase are higher when the laser is polarized along the axis of the dimer, compared to the case when the laser is polarized perpendicularly to the axis of the dimer.

To investigate further, 3D FEM simulations are performed. Results are shown in Figure 3D. The left side of Figure 3D shows the electrical field enhancement factor (EEF) when the laser is polarized along the axis of the dimer, whereas the right side shows the EEF in the case when the laser is polarized perpendicularly. The significant increase of EEF when the polarization is along the axis of the dimer points to stronger LSPR coupling through the nanogap between the two AuNSs. This also means that there is increased plasmonic heating due to stronger absorption of incident laser in this polarization. To quantify, a polarization-dependent heating ratio is calculated to be 2.7 for the simulated model. An experimental polarization-dependent heating ratio of 2.3 is obtained. The good agreement between heating ratios obtained experimentally and by simulation indicate the validity of the experimental method to probe plasmonic heating. The minor difference between experiment and simulation can be attributed to the following: (i) in the simulation, the geometry of the AuNS is assumed to be perfectly symmetrical with a smooth surface. However, as the SEM image in Figure 3A (right) shows, the dimer probed in the experiment are asymmetric with a rough surface. Identical and perfectly spherical AuNSs should result in higher heating ratio due to a more predictable difference in the LSPR coupling behavior for the two orthogonal incident polarizations.⁴⁰ (ii) A nanogap of 2 nm is assumed for the purpose of simulation, however, it is very difficult to determine the actual size of the nanogap from the SEM image. (iii) The simulation considers the two polarization directions to be perfectly orthogonal. In the experiment, this might not exactly be the case since manually controlling rotation of the string (and with it, the probed particles) with respect to the polarization of the incident laser could introduce error. (iv) The roughness of the string may influence the interference pattern of the laser near the probed NPs. In

the simulation, the surface of the string is assumed to be smooth. Note that for the dimer case, part of the polarization-dependent heating difference should come from the shape anisotropy. However, since the observed difference in polarization-dependent heating of the dimer is much larger than that of the monomer, the different optical absorptions caused by the two polarization-dependent plasmon modes are expected to be the major contributors to the difference in heating.

Probing local heating of shell-isolated Au NPs: Shell-isolated Au NPs have recently gained much interest because of their high detection sensitivity and their applications in plasmon-assisted nanochemistry, photothermal cancer therapy and SERS.^{7,30} Following the same experimental procedure as detailed in the previous section, a single shell-isolated Au NP, as shown in Figure 4A (left), is first probed. Results are shown in Figure 4B. As expected, a linear relationship is observed.

Figure 4. (A) SEM images of the probed single shell-isolated Au NP and its dimer. (B, C) The relative frequency shift Δf and the corresponding maximum temperature increase ΔT_{max} versus incident laser power for (B) single and (C) dimer of shell-isolated Au NPs under two orthogonal polarizations. The insets show representative photothermal images

depicting the decrease in resonance frequency on the SiN strings under both polarizations. (D) Simulated EEF across the center plane of a shell-isolated Au NP dimer on SiN under the two polarizations at 633 nm excitation.

Next, we probe polarization-dependent photothermal heating of a dimer of shell-isolated Au NPs (Figure 4A, right). Results are shown in Figure 4C. In particular, the heating is higher when the polarization direction is along the axis of the dimer. This is similar to the case of an AuNS dimer. Simulation results in Figure 4D show that the maximum EEF is higher when the laser polarization is along the dimer axis than when it is perpendicular to the dimer axis. This suggests stronger LSPR coupling in the former case, and as a consequence, stronger plasmonic heating. The experimental and simulated polarization-dependent plasmonic heating ratios are calculated to be 1.8 and 2.2, respectively. The difference in the two ratios can be attributed to the following: (i) The presence of the silica shell in the experiment introduces additional thermal mass. This would lead to a reduced temperature contrast on the SiN string for the two polarizations. (ii) Points (iii) and (iv) discussed in the previous section. Additionally, the heating ratio between the two polarizations for the dimer of shell-isolated Au NPs is comparatively lower than that for the AuNS dimers. This can be mainly attributed to the presence of the silica shell, which creates a larger nanogap (~30 nm) that reduces the strength of LSPR coupling.

Probing local heating of Au nanostars: Au nanostars are another interesting set of particles that are widely used for various applications due to the lightning rod effect of the tips which generate nanoscale EM hot spots in their very close vicinities.^{41–43} To investigate plasmonic heating of Au nanostars, a single Au nanostar, shown in Figure 5A (left), is probed first. Figure 5B shows the linear response of Δf and ΔT_{max} with increased laser power. The plot shows slightly different heating in the two polarizations. However, after normalization by taking into account the fraction of laser power that leads to the frequency shifts, the polarization-dependent heating ratio becomes ~1.0. The plasmon resonances of a nanostar result from the hybridization of plasmons associated with the core and the individual tips. Although the shape anisotropy is large for a nanostar, its plasmon resonance wavelengths are not sensitive to polarization.⁴⁴ In addition, the strengths of its resonances are associated with the size of the tips and the polarization.⁴⁴ In our case, since the tips of the probed nanostar have similar sizes, plus that the excitation wavelength is away from the plasmon resonance wavelength, an observed polarization-dependent heating ratio of ~1.0 is reasonable. Next, a dimer of Au nanostars (Figure 5A, right) is probed under two orthogonal polarizations. Results are shown in Figure 5C. Although the heating in both polarization directions looks very similar in Figure 5C, after normalization, the polarization-dependent heating ratio becomes 1.2. This value is much smaller

compared to both the AuNS dimer and the shell-isolated Au NP dimer cases. This could be caused by (i) larger gap distance between the two Au nanostars, (ii) much stronger LSPR at the tips due to the lightning rod effect than that generated via the couplings through the nanogap,⁴⁵ and (iii) large deviation of the excitation wavelength from the LSPR wavelength for the nanostar case.

Probing local heating of AgNCs: The last set of particles probed is the AgNC. In the past decade, nanocube or nanocage structures have been receiving much attention due to their applications in metal-enhanced fluorescence in biological systems,⁴⁶ photothermal destruction of cancer^{47,48} and drug delivery.⁴⁹ We begin with a single AgNC shown in Figure 6A (left). The single AgNC is probed at four laser powers along two polarization directions, i.e., along the sides and along the diagonal line of the AgNC. Figure 6B plots δf and $\Delta T_{\max}$ for both polarizations with respect to laser power. A polarization-dependent heating

images depicting the decrease in resonance frequency on the SiN strings under the two polarizations.

ratio of 1.2 is obtained. Note that the simulation of a perfect single AgNC (Figure 6C) shows a polarization-dependent heating ratio of 1.0. This is expected, since the diagonal LSPR mode can be regarded as the superposition of two symmetric LSPR modes oscillating along the sides of the AgNC. The difference in the ratios between the experiment and the simulation can be ascribed to (i) the different shape and sharpness of the corners for the experimentally probed AgNC, and (ii) inaccuracy in change of polarization direction in the experiment, due to manual alignment. A dimer comprising of two closely spaced single AgNCs is probed next. The dimer is shown in Figure 6A (right).

Figure 5. (A) SEM images of the probed Au nanostar monomer and dimer. (B, C) The relative frequency shift δf and the corresponding maximum temperature increase $\Delta T_{\max}$ versus incident laser power under two orthogonal polarizations for (B) a single Au nanostar and (C) an Au nanostar dimer. The insets show representative photothermal

Figure 6. (A) SEM images of the probed AgNC monomer and dimer. (B) The relative frequency shift δf and the corresponding maximum temperature increase $\Delta T_{\max}$ versus incident laser power under two polarizations for a single AgNC. (C) Simulated EEF across the center plane of an AgNC on SiN under two polarizations at 633 nm excitation. (D) The

relative frequency shift δf and the corresponding maximum temperature increase $\Delta T_{\max}$ versus incident laser power under two polarizations for an AgNC dimer. (E) Simulated EEF across the center plane of an AgNC dimer on SiN under two polarizations at 633 nm excitation. The insets in (B) and (D) show representative photothermal maps depicting the decrease in resonance frequency on the SiN strings under different polarizations.

Results are shown in Figure 6D. It can be seen that δf and $\Delta T_{\max}$ vary linearly with laser power. In addition, the AgNC dimer generates more heat when the polarization of the laser is along its axis compared to the perpendicular case. The simulated EEF is plotted in Figure 6E. It shows that the LSPR is stronger when the polarization is along the dimer axis, resulting in more heating. The polarization-dependent heating ratio obtained experimentally is 1.3 whereas the simulated value is 1.2. The slight difference in ratios can be attributed to (i) error introduced by manual alignment of laser polarization with respect to the AgNC dimer axis, (ii) different shape and sharpness for the corners of the probed AgNC dimer, and (iii) size of the nanogap being different in the simulation and in the experiment due to difficulty in its determination from the SEM image.

Optical absorptions of probed NPs: The experimentally quantified and the simulated absorption cross sections of the different types of NPs probed are plotted in Figure 7. The good agreement between the experiments and the simulations indicates the validity of the experimental method and the developed data analysis model to measure optical absorption cross sections of single NP and NP dimers. The slight difference in the absorption cross sections between the experiments and the simulations could be due to (i) surface roughness and shape deformation of the experimentally probed NPs, (ii) roughness of the string, which may influence the interference pattern of the laser near the probed NPs, (iii) errors in the simulation, since the exact sizes of the nanogaps are difficult to determine from the SEM images, and (iv) experimental errors, such as polarization alignment and focus of the laser. In addition, absorption spectra of monomers and dimers of Au NS and shell-isolated Au NPs on SiN are simulated and plotted in Figure S3 in the supplementary. It can be seen from Figure S3 that the SiN substrate causes strong red shifts to plasmon resonances of Au spherical nanoparticles due to its high refractive index. Also, the wavelength of excitation (633 nm) is far from the plasmon resonance wavelengths, for all the cases. This reveals that the method can be used for quantification of optical absorption cross sections of individual plasmonic structures whose LSPR wavelengths are far from that of the excitation wavelength. This is attributed to the excellent sensitivity of the method (~ 89 Hz/K).

Figure 7. The experimental and the simulated absorption cross sections of the different types of NPs on SiN string resonators under different polarization directions of excitation.

CONCLUSION

In conclusion, we have demonstrated the use of SiN micromechanical string resonators as an excellent tool for profiling optical absorption cross sections of individual plasmonic NPs and their dimers, even of those consisting of extremely small nanogaps or exhibiting LSPR wavelengths far from the excitation. Our results shed light on the thermoplasmonic behavior of the probed NPs and illustrate that the plasmonic heating is strongly influenced by the actual particle geometry and morphology. Moreover, the developed method and the obtained optical absorption profiles of the different NPs with different configurations facilitate future development and optimization of thermoplasmonic applications. Our work not only facilitates a better fundamental understanding of thermoplasmonics, but also opens up new avenues for the application of these nano-sources of heat.

ASSOCIATED CONTENT

Supporting Information. Experimental results demonstrating the (i) relative frequency shift of a bare string irradiated by a 633 nm laser and (ii) relative frequency shifts of a blank quartz fragment and the same piece but covered with an AuNS dimer.

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.

Author Contributions

The manuscript was written through contributions of all authors

Funding Sources

This work was supported by the Danish National Research Foundation (Project DNRF122) and Villum Fonden (Grant No. 9301).

ACKNOWLEDGMENT

The authors would like thank Dr. Chiara Mazzoni for her help on SEM characterizations and Dr. Peter Ouma Okeyo for his help in preparing the quartz sample. The authors would also like to thank the cleanroom staff at the National Centre for Nano-Fabrication and Characterization at the Technical University of Denmark (DTU Nanolab), especially process specialist Dr. Karen Birkelund, for her extensive guidance.

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