Enhanced Raman Scattering for Probing Near-Field Distribution in All-Dielectric Nanostructures

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Resonant all-dielectric nanophotonic structures have recently demonstrated enhancement of light emission and localization of near-fields outside and inside the nanoresonators of various functionality. However, probing of the near-field is still a time-consuming and challenging procedure, requiring near-field optical microscopy or cathodoluminescence approaches. On the contrary, inherent light emission such as Raman scattering from all-dielectric nanostructures can provide important information on their resonant properties. Herein, probing of near-field spatial distribution around a silicon trimer qualitatively using far-field excitation of Raman scattering is demonstrated. The geometry of a single excitation and collection objective with lateral scanning is implemented. With this technique, switching near-field distribution in the silicon trimer by changing the polarization of the incident light is observed. The full-wave numerical simulations support the observed experimental results. It is believed that such an approach will be useful for near-field probing of various all-dielectric resonant nanostructures with a simple far-field optical scheme.

1. Introduction

All-dielectric nanophotonics is an extensively growing area of optics that studies light–matter interactions in nanoscale objects, which usually support resonances in the visible range[1,2] thus allowing advanced light harvesting and manipulation and enhancement of the intrinsic processes. Since the very first experimental observation of optical resonances in the simplest semiconductor nanostructure, nanosphere,[3,4] a lot of attention was brought to the so-called Mie-nanoresonators[5,6] that support optical modes of the both nature—electric and magnetic ones—allowing for practical realization of unidirectional scattering,[7–9,11] enhancement of nonlinear response,[12–14] localized phase change,[15] photoluminescence,[16–18] lasing,[19,20] and sensing.[21–27] However, probing of near-field is still a time-consuming and challenging procedure, requiring near-field optical microscopy[28] or cathodoluminescence approaches.[29] On the contrary, it was previously shown that Raman scattering[30] can be used for detecting optical states, either nonradiating[31,32] or bright modes (radiating) of the different order.[33,34]

In this work, we propose a method based on Raman microspectrometry for optical far-field probing of near-field features in a complex resonant silicon nanostructure. We show numerically simulated and prove experimentally that the field maxima inside a silicon trimer can be probed via linear inelastic scattering on optical phonons, i.e., with Raman scattering. We believe that the revealed approach can be further extended to other all-dielectric designs and would benefit from the Raman technique that allows one to simultaneously optically heat nanostructures and measure their temperature in real time by the spectral shift of the Stokes signal,[35] where thermally nonlinear photonic state switching[36–38] might take place.

2. Results and Discussion

2.1. Far-Field Analysis

To perform the measurements, we fabricate nanodisks on a glass substrate made of amorphous silicon film of 165 nm thickness (see Experimental Section for details). The scanning electron microscopy (SEM) measurements allow us to control the diameter of all fabricated structures (see corresponding insets of Figure 1).

Since the observation and existence of the field enhancement in nanophotonic structures depend on the excitation of optical resonant modes in single nanoresonator, we begin our consideration with studying single nanodisks and their optical scattering properties. Figure 1a shows both experimental and numerical spectra of dark-field scattering (see details of measurements and calculations in Experimental Section) for single a-Si:H nanodisks of 420 nm diameter on a glass substrate. The schematic illustration of the excitation and signal collection in the dark-field scheme for the nanodisk is shown in Figure 1b. Particular interest in such structures is mainly caused by their ability to support resonant optical states in the visible range and especially nearby the HeNe laser central wavelength of 632.8 nm which was
Figure 1. Dark-field scattering spectra. a) Numerical simulation and experimental scattering spectra of a single a-Si:H nanodisk with 420 nm diameter and 165 nm height and c) an oligomer consisting of three similar nanodisks. Solid blue lines correspond to experimental dark-field scattering spectra, dashed blue lines correspond to numerically calculated data on scattering intensity, and red dotted data correspond to electric energy inside the nanodisks. The SEM images of the disks are shown in the upper left insets. Scale bars are 200 nm. Red dashed lines correspond to 632.8 nm wavelength of a HeNe laser. b,d) Schematic of the dark-field spectroscopy setup for single nanodisk and oligomer.

2.2. Simulations of Raman Response

The Raman photons emission from silicon nanostructures is provided by the scattering of pumping photon with the lattice phonons. In a classical picture, that can be explained in appearance of local Raman polarization \( P_R \) induced at the frequency shifted from the pump frequency \( \omega \) for the Stokes frequency \( \Omega_S \). This polarization is defined by the Raman polarizability tensor and amplitude of the local field \( \mathbf{P}_R(r, \omega, \omega - \Omega_S) = \hat{\alpha}^{R}(r, \omega, \omega - \Omega_S) \mathbf{E}(r, \omega) \). While the tensor structure is defined by the material properties, one can obtain that for noncrystalline structure the intensity of Raman emission is provided by two factors: 1) intensity of the pumping field and 2) Purcell factor corresponding to Stokes signal emission in accordance to following expression\(^{[19]}\)

\[
\langle I_R \rangle \sim \int dV F_p(\omega - \Omega_S, r) |P_R(r, \omega, \omega - \Omega_S)|^2 \\
\sim \int dV F_p(\omega - \Omega_S, r) |E(r, \omega)|^2
\]

(1)

where \( F_p(\omega - \Omega_S, r) \) is the Purcell factor and integration is taken over the volume of nanostructure.

To separate these two factors and their contribution, we first plot the field enhancement at the excitation wavelength in a single disk and trimer structure. In Figure 2a, the distribution...
Figure 2. Calculated near-field and Purcell factor spatial distributions. Calculated distribution of the pumping field in a) single disk and b) oligomer structure excited by a plane wave at 632.8 nm with polarization direction shown in the figure. The color scale bars are normalized by the magnitude of the incident $E_0$. Red and white arrows show the directions and magnitude of magnetic and electric dipole moments correspondingly. c) The calculated Purcell factor for dipole emitter of different polarizations is shown as function of distance $s$. The location and dipole polarization are shown in the inset. The disk diameter, height, and gap equal to 420, 165, and 30 nm, respectively.

of the field intensity in a single nanodisk is shown. The plane wave excitation at 632.8 nm with polarization along z-axis provides 9 times enhancement light intensity. In the case of a trimer nanostructure irradiated under the same conditions, near-field structures in the upper two disks are almost the same, but the hotspot with the enhancement up to 4.5 times is additionally formed between the two upper nanodisks (Figure 2b). At the same time, intensity enhancement in the lower disk appears to be much weaker. Obviously, plane wave polarization along y-axis will result in similar field enhancement effects but for right nanodisks. Remarkably, according to the results of our calculation, the structures with the least gap in between nanodisks (30 nm resolution achievable for the used technique) and 420 nm diameter possess the most pronounced difference in measured Raman intensities for different polarizations. Multipole decomposition performed numerically (see details on calculation method elsewhere[5]) reveals the dominant role of magnetic dipole resonances in each nanodisks forming the near-field distribution upon 632.8 nm irradiation (Figure 2b). The magnetic and electric dipole moments are shown with red and white arrows, respectively, in Figure 2a,b.

The contribution of the second factor related to the emission of Stokes photons is defined by the density of optical states. The corresponding Purcell factor is shown in Figure 2c at emission wavelength 654 nm corresponding to Stokes photons. The Purcell factor is calculated at the line connecting centers of two nanodisks at the middle of their height for three different polarizations of dipoles by direct numerical modeling in Comsol Multiphysics. One can see that the Purcell enhancement is observed close to the nanodisks centers. At the same time, a strong enhancement is also observed in the gap between the disks for z-polarization of dipole, however, it does not contribute to Raman emission enhancement as there are no Raman sources.

Though Figure 2 is plotted for plane wave excitation case, in the experiments a sharply focused laser beam is used. Thus, one need to take into account excitation field distribution with Gaussian beam profile: $|E_0(r,z)|^2/(2\eta) = I_0 (\omega_0/\omega(z)) \exp(-2r^2/(\omega(z))^2)$, where $I_0$ is the intensity in the beam center, $r^2 = (x-x_0)^2 + (y-y_0)^2$ is the distance from the beam center at $(x_0, y_0)$, $\omega(z)$ is the beam waist, $\omega_0$ is the beam waist at the focal spot that is defined by the Rayleigh range at a given wavelength, and $\eta$ is the impedance of the free space with normal incidence with respect to the substrate for calculation of total integral of power density stored in all three nanoresonators. Taking into account the field profile allows one to predict the intensity distribution of Raman signal across the sample because the intensity of Raman scattering is proportional to the squared field magnitude of the excitation field.

2.3. Raman Spectroscopy

Hydrogenated amorphous silicon (a-Si:H) has a pronounced Raman response with a broadened Stokes line at 480 cm$^{-1}$[10], thus providing an opportunity to conduct Raman microspectroscopy of the fabricated nanostructures in a standard confocal optical scheme.

First, we study Raman response of a single resonant nanodisk with 420 nm diameter placed on a glass substrate. The HeNe laser of $\lambda = 632.8$ nm central wavelength is sharply focused on the sample with a beam width of 1.22$\lambda$/NA, where NA is the numerical aperture of the objective equal to 0.9 (for more details, see Experimental Section). The setup allows one to precisely vary the beam focus position with respect to the sample with piezo-stage and conduct the separate measurement of the Raman scattering.

Despite Raman signal has usually rather low intensity, the matching of optical resonances with pump or emission wavelengths (see Figure 1a,c) results in the signal enhancement[33,39] and, thus, sub-1-second level of acquisition time. This is important for the nanostructures mapping with high spatial resolution and single step of piezo-stage around 50 nm, which is 900 steps for each map. Thus, the Raman intensity is observed in the region furthest from the samples— with $(x,y)$ coordinates of $(-750, -750)$ nm—which is enough to go away from the sample by the focused laser beam. As the structure is symmetric to the rotation along the z-axis, we also expect no difference in Raman intensity map for different directions of the focused beam scanning. Figure 3 shows the experimentally measured map of Raman scattering intensity on the area of $1.5 \times 1.5 \mu$m$^2$ when
Figure 3. Experimental measurement of near-field response. Raman scattering intensity mapping for different laser beam position along x-y plane of oligomer nanostructure for a) x- and b) y-oriented polarization of E-field of the incident laser at wavelength 632.8 nm. Calculated absorbed electromagnetic power by oligomer structure for different Gaussian beam position at wavelength 632.8 nm for c) x and d) y polarization of the E-field. e) Experimental Raman scattering spectra of an oligomer structure corresponding to the laser position 1 and 2 from part (b). Signal acquisition time is 0.25 s. f) Schematic of the hotspot excitation indicating the origin of different signal intensity in the Raman spectra shown in part (e).

the polarization of incident light is horizontal (Figure 3a) and vertical (Figure 3b) relatively to the orientation of the picture, as also schematically shown in Figure 3e,f. One can see that the polarization rotation results in considerable shift of the Raman signal maximum in space.

The results for such calculations with account for the incident Gaussian intensity profile corresponding to the experimental beam size are shown in Figure 3c,d. The maps depict the normalized magnitude of the total power stored inside all three nanodisks for different beam position with respect to the sample and with similar step of the “scan.” The comparison of the numerical simulation and experimental maps reveals good qualitative agreement between them. The position of signal maximum for all cases between two neighbor nanodisks is the result of overlapping the enhancements from the maxima in the centers of the nanodisks (see schematic illustration in Figure 3f). Reason of the overlapping is the Gaussian beam diameter ($\approx \lambda$), which is comparable with the nanodisks size. Nevertheless, the proposed approach allows us to clearly reveal polarization dependence of the near-field distribution. Thus, the proposed Raman-based far-field technique can be applied for qualitative analysis of the nanostructure near-field spatial distribution with polarization control.

3. Conclusion

In this work, we have shown far-field probing of near-field distribution in a resonant silicon nanostructure by means of Raman scattering coming from the studied material. Namely, we have identified the regions in a silicon trimer where near-field is enhanced for different polarization of the incident field with spatial resolution close to the diffraction limit. Remarkably, the demonstrated approach does not require any deposition of additional light-emitting materials (e.g., dyes or quantum dots) for near-field visualization. Because the Raman is thermally sensitive process, we believe that such approach will be applicable for broad range of investigations, including thermally induced nonlinearities, sensing, and nanothermometry.

4. Experimental Section

Samples Fabrication: Nanodisks were made of $\alpha$-Si:H on a glass substrate. The fabrication of amorphous nanodisks with diameters $D = 420 \text{ nm}$ and height $h = 165 \text{ nm}$ was conducted using electron-beam nanolithography technique. The sample images were obtained using a SEM (Carl Zeiss, Neon 40).

Dark-Field Scattering Spectra Measurements: To conduct measurements of scattering spectra, we apply a dark-field scheme, where an infinity corrected objective ($10 \times NA = 0.26$, Mitutoyo Plan Apo NIR) is used for illumination with a white light source (HL-2000 halogen lamp) of the sample under angle $67^\circ$ to the surface normal. The second objective ($50 \times NA = 0.42$ Mitutoyo Plan Apo NIR) placed perpendicularly to the sample surface is applied for scattering signal collection. The scattered signal is analyzed by a confocal system with a spectrometer (HORIBA LabRam HR) and cooled CCD Camera (Andor DU 420 A-OE 325) equipped with a 150 g mm$^{-1}$ grating. The position of the nanoparticles is controlled by an additional CCD camera (Cannon-400 D). For more details and schematic of the setup, see Section S1, Supporting Information.
Raman Scattering Measurements: The Raman spectra measurements were conducted utilizing the same registration system (HORIBA LabRam HR), but with a 600 g mm\(^{-1}\) diffraction grating and 632.8 nm HeNe laser as a light source focused through a microscope objective (100 × NA = 0.9 Mitutoyo Plan Apo HR) to the sample surface. The same objective is used for excitation and collection of the Raman signal. The sample with nanoparticles is placed on a piezo-stage (AIST-NT) providing a positioning accuracy of 10 nm during a thermal imaging process. For more details and schematic of the setup, see Section S1, Supporting Information.

Numerical Calculations: Numerical simulation description of scattering spectra of silicon nanoparticles on a glass substrate as well as their absorption performance was conducted numerically in a commercial software Comsol Multiphysics. The collecting aperture for elastic scattering signal was adopted from experimental setup and equals to NA = 0.42. Diameter of computational domain is chosen to be 3μm. The bottom hemisphere plays a role of a substrate, when we consider inhomogeneous surrounding of the particle, whereas it is similar to the upper hemisphere in the case of homogeneous surrounding. For absorption calculation, the incident light source was 632.8 nm Gaussian beam, whereas for scattering in the range 400–1000 nm plane wave excitation was considered.

The simulations of Purcell factor spectra were obtained by explicit calculations in Comsol Multiphysics. A dipole emitter with fixed dipole moment was placed inside the nanostructure and its position was varied across the nanodisks. The emitted total electromagnetic power \( P \) was computed by integrating the Poynting vector across the sphere containing the structure. To obtain the Purcell factor, the computed power \( P \) was normalized to power emitted in vacuum \( P_0 \) by a dipole of the same amplitude:

\[
P_p = \frac{P}{P_0}.
\]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

nanophotonics, near-field distribution, optical resonances, Raman scattering, silicon
[30] I. Alessandri, J. R. Lombardi, *Chem. Rev.* **2016**, *116*, 14921.
[31] D. G. Baranov, R. Verre, P. Karpinski, M. Käll, *ACS Photonics* **2018**, *5*, 2730.
[32] K. V. Baryshnikova, K. Frizyuk, G. Zograf, S. Makarov, M. A. Baranov, D. Zuev, V. A. Milichko, I. Mukhin, M. Petrov, A. Evlyukhin, *JETP Lett.* **2019**, *110*, 25.
[33] P. A. Dmitriev, D. G. Baranov, V. A. Milichko, S. V. Makarov, I. S. Mukhin, A. K. Samusev, A. E. Krasnok, P. A. Belov, Y. S. Kivshar, *Nanoscale* **2016**, *8*, 9721.
[34] G. P. Zograf, M. I. Petrov, D. A. Zuev, P. A. Dmitriev, V. A. Milichko, S. V. Makarov, P. A. Belov, *Nano Lett.* **2017**, *17*, 2945.
[35] M. Balkanski, R. Wallis, E. Haro, *Phys. Rev. B* **1983**, *28*, 1928.
[36] J. Berzinš, S. Indrišūnas, S. Fasold, M. Steinert, O. Žukovskaja, D. Cialla-May, P. Gečys, S. M. Bäumer, T. Pertsch, F. Setzpfandt, *Opt. Express* **2020**, *28*, 1539.
[37] Y.-S. Duh, Y. Nagasaki, Y.-L. Tang, P.-H. Wu, H.-Y. Cheng, T.-H. Yen, H.-X. Ding, K. Nishida, I. Hotta, J.-H. Yang, Y.-P. Lo, K.-P. Chen, K. Fujita, C.-W. Chang, K.-H. Lin, J. Takahara, S.-W. Chu, *Nat. Commun.* **2020**, *11*, 1.
[38] T.V. Tsoulos, G. Tagliabue, *Nanophotonics* **2020**, *9*, 3849.
[39] K. Frizyuk, M. Hasan, A. Krasnok, A. Alú, M. Petrov, *Phys. Rev. B* **2018**, *97*, 085414.
[40] I. Staude, V. V. Khardikov, N. T. Fofang, S. Liu, M. Decker, D. N. Neshev, T. S. Luk, I. Brener, Y. S. Kivshar, *ACS Photonics* **2015**, *2*, 172.