Quantitative Measurement of the Near-Field Enhancement of Nanostructures by Two-Photon Polymerization

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Supporting Information

ABSTRACT: The quantitative determination of the strength of the near field enhancement in and around nanostructures is essential for optimizing and using these structures for applications. We combine the Gaussian intensity distribution of a laser profile and two photon polymerization of SU 8 to a suitable tool for the quantitative experimental measurement of the near field enhancement of a nanostructure. Our results give a feedback to the results obtained by finite difference time domain (FDTD) simulations. The structures under investigation are gold nanotriangles on a glass substrate with 85 nm side length and a thickness of 40 nm. We compare the threshold fluence for polymerization for areas of the Gaussian intensity profile with and without the near field enhancement of the nanostructures. The experimentally obtained value of the near field intensity enhancement is 600 ± 140 , independent of the laser power, irradiation time, and spot size. The FDTD simulation shows a pointlike maximum of 2600 at the tip. In a more extended area with an approximate size close to the smallest polymerized structure of 25 nm in diameter, we find a value between 800 and 600. Using our novel approach, we determine the threshold fluence for polymerization of the commercially available photopolymerizable resin SU 8 by a femtosecond laser working at a wavelength of 795 nm and a repetition rate of 82 MHz to be 0.25 J/cm^2 almost independent of the irradiation time and the laser power used. This finding is important for future applications of the method because it enables one to use varying laser systems.

Metallic nanostructures are used in various applications such as SERS,¹ high resolution lithography,^{2,3} and surface chemistry.⁴ As qualitative experiments have shown, the strength of the near field enhancement (NFE) is strongly dependent on shape and environment of the nanostructure.^{5–7} Especially the difference in shape between the nanostructures used in simulations and experiments can give rise to strong deviations of the NFE.⁶ For the development of a comprehensive understanding of the near field and a versatile method for its determination, the quantitative and qualitative results obtained by experiment and calculations (like finite difference time domain simulations (FDTD)^{3,5,8,9} and discrete dipole approximations (DDA)^{6,11}) have to be combined. A well tested way to measure the strength of the near field enhancements of nanostructures is a near field scanning optical microscope (NSOM), where the emitted light in the near field is collected by a scanning tip at a small distance of some nanometers away from the structure.^{12,13} As the interaction between nanostructures with a distance below the decay length of the near field can significantly alter the near field distribution and resonance of these structures,^{14–16} a modification of the NFE has to be considered. This makes the determination of the near field enhancement particularly interesting and challenging.

In response to this problem, several methods with high spatial resolution that give qualitative information on the spatial dependence of the near field distribution around nanostruc-

tures without an interacting probe, such as photoemission electron microscopy (PEEM¹⁷), electron energy loss spectroscopy (EELS¹¹), phase change materials¹⁸ and direct ablation of a substrate,¹⁹ have been put forward. Recently, Deeb et al.²⁰ have shown that a specially tailored molecule can be used to obtain the near field enhancement of round silver nanoparticles with sub 10 nm resolution by atomic force microscopy (AFM). They determined an intensity enhancement of this special geometry of 34.

Another way to visualize the NFE of nanostructures relies on the photoresponse of the resin SU 8^{3,8,9,21} operated in the highly nonlinear regime where two photon polymerization (TPP) occurs. Using this material, Sundaramurthy et al.³ were able to obtain an intensity NFE of 61 between gold nanotriangles of 80 nm side length and a titanium adhesion layer by applying tightly focused femtosecond laser pulses at 800 nm and comparing laser shots with different power. However, since the underlying mechanism is highly nonlinear, other potential influences of the experimental parameters, as, for example, the repetition rate of the laser, have to be

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considered to develop a versatile and reliable method suitable for applications with variable optical systems.

Here, we present a further improvement of this method for the quantitative measurement of the NFE with SU 8 by using a single laser pulse (or also a sequence of pulses) with a Gaussian intensity profile. This method is much faster and independent of the absolute power of the laser in use.

In case of SU 8, a nonlinear two photon process links together the polymer chains.²² For the TPP, a certain threshold fluence has to be exceeded.^{23,24} This process allows highly resolved scanning electron microscopy (SEM) images^{25,26} with a contrast tunable by the choice of the imaging electron energy and spatial resolution of below 30 nm [ref 3] by using a commercially available and well established polymer. In general, the threshold fluence of SU 8 depends on the repetition rate of the used femtosecond laser,²⁴ as a thermal heat load can lead to increased cross linking of the polymers.²⁷ Typical values range from 0.4 to 1 J/cm² for a repetition rate of 25 to 5 MHz.²⁸

Unfortunately, this method is not without drawbacks for the quantitative measurement of the near field enhancement, as the two photon process depends on various factors including the concentration of the photoinitiator molecules in the mixture,²³ temperature,²⁷ and a change of the nonlinear mechanism as a function of the intensity of the laser beam.²⁸ The exact exponent p of the power dependence of the polymerization threshold is not known and might vary from batch to batch of the resin. In light of these limitations, we developed a method, where a laser with a Gaussian intensity distribution irradiates a sample covered with an array of nanostructures. In our case, we used flat, triangular nanoprisms, arranged in hexagonal networks, as they can be prepared in a straightforward way by means of colloid lithography.²⁹ After development and postprocessing of the sample, two areas with the same fluence, namely, the threshold fluence, are compared. One area is chosen such that this fluence is reached on the bare surface, for example, in the hexagons formed by the arrangement of the triangles (i.e., without NFE), and the other is where it is reached at the tips of the triangles due to the NFE effect. Thus, the details of the actual mechanism and nonlinearities of the polymerization of SU 8 cancel out and the NFE is calculated by comparing the irradiation intensities of the areas. In the following, we will discuss the NFE in terms of *intensity*.

■ EXPERIMENTAL DETAILS

In this experiment, we use a Gaussian laser beam to irradiate the resin SU 8. By comparing the threshold fluence for different regimes of the array of the nanotriangles, we determine the intensity NFE factor α of the triangles. Thus, a precise knowledge of the Gaussian intensity distribution on the surface is important. Figure 1 shows a typical intensity distribution on the surface obtained by an optical microscope and the corresponding fwhm as function of displacement of the lens out of its focal point in the beam direction (for details see Experimental Section below).

After irradiation and development of the substrate with the chosen beam profile, the polymer structure looks as it does in Figure 2 (middle panel). We can distinguish three main areas labeled A, B, and C in Figure 2: (i) In the center, a domelike structure can be seen (region A), in which polymerization takes place even without the help of NFE. In this region, the resin changes into a very thin polymer layer covering the complete surface (Figure 2, middle and lower part). (ii) In the ring shaped region B surrounding region A polymerization is observed at the tips of the triangles where strong NFE occurs. In this region, no polymerization is observed in the hexagons between the triangles. (iii) Finally, there is a third region (C), in which no polymerization at all is observed.

Figure 1. Measured fwhm of the slightly elliptical laser spot on the surface for a shift of the lens position of the optical setup out of the optimum by Δf . The insets show the captured image of the laser spot and the profile of the shorter vertical axis for two specific lens positions indicated by the red arrows.

Figure 2. Intensity profile of the incident laser beam on the surface with the threshold fluences for polymerization without any NFE of the structures (A, blue dashed line) and due to the NFE (B, red dashed line) is illustrated in the upper panel. In area C, no polymerization occurs anymore. To illustrate the method, the same boundaries are drawn into the SEM images. In the middle panel, an SEM image of a polymerized area irradiated by a Gaussian laser beam with a fwhm of 15.2 μm is shown. In the circle in the center of the laser beam, where the surface appears black, the intensity is high enough to polymerize the SU 8 in a domelike structure, and in the very center the metallic nanostructures have been ablated.³⁰ This area is not of importance for the determination of the NFE. Blow ups of the threshold regions are shown in the lower part of the figure. The scale bars in the lower part are 2 μm (right) and 600 nm (left).

We now discuss the transition between regions A and B, then between B and C. The intensity at the threshold between regions A and B, indicated in Figure 2 by a blue circle, is defined as I_1 . We choose the intensity such that this threshold occurs typically at less than half of the maximum fluence in the center of the laser spot. From the FDTD calculations in Figure 5, one can see that there is no NFE in the hexagonal area between the triangles, where the colloids resided (i.e., the enhancement factor $\alpha = 1$), meaning that the incident laser intensity leads to polymerization in this region. The incident fluence I_1 at this radius r_1 equals the threshold fluence $I_{\text{threshold}}$ for polymerization at the used irradiation time. By using SEM, r_1 is measured and using the known laser profile, the fluence I_1 is determined. Outside this

region A with radius r_1 , the polymerization at the triangles is due to the near field enhancement α of the incident laser intensity. The intensity at the threshold between B and C is labeled I_2 . The position of this threshold is indicated by the red circle with the radius r_2 . At this radius, the fluence I_2 of the laser beam is amplified by the NFE α such that it

Figure 3. Development of the polymerization (green areas in illustration and gray areas in the SEM images) around the gold triangles (orange in illustration, light gray in the SEM images) with decreasing intensity from left to right is shown in more detail. The blue and red lines correspond to the boundaries defined in Figure 2. In part I, a sketch illustrates the different stages and the corresponding threshold fluences. For simplicity only pairs of triangles are represented in areas B and C (to the right side from the blue line). In panel II, a typical triangle at the threshold of polymerization can be seen. In part III, a SEM image, taken at a location with a steep intensity gradient, shows the polymerization around the nanotriangles at the threshold for polymerization with the NFE of the triangles. The polymerized structure at the tip is 25 nm wide. The scale bars are 100 nm in II and 200 nm in III. The white arrow indicates the polarization direction.

equals the threshold fluence $I_{\text{threshold}}$. As indicated in Figure 3, part III, the size of the polymerized structures around the triangles decreases with decreasing laser intensity until the laser fluence enhanced by the near field is below the threshold for polymerization and no SU 8 is polymerized at the tips (Figure 2, lower panel, red line). Analogously to the fluence I_1 , the fluence I_2 is obtained by analyzing the SEM pictures, the irradiation time and the intensity distribution of the laser profile (Figure 1). In Figure 3, III, this change in the size of the polymerized area at the tip is shown using a laser profile with a steep gradient in the intensity of the laser.

This way, we have obtained the fluence I_1 , which represents the threshold fluence for polymerization directly, and I_2 , which matches $I_{\text{threshold}}$ only due to the near field enhancement α at the tip. With these two fluences the near field enhancement α at the tip can be calculated by

$$\alpha = I_1/I_2 \quad (1)$$

The exact knowledge of the exponent $p \leq 2$ for the two photon process, which is proportional to I^p , is not important as the same fluences $I_{\text{threshold}}$ are compared in order to obtain the enhancement α of the near field intensity. To investigate a potential dependence of the NFE on the laser power and the fwhm of the laser profile, these two parameters have been varied throughout different experiments and the irradiation time has been adapted to realize the required laser fluence.

RESULTS

In the following experimental and simulated results, 40 nm thick gold nanotriangles with 85 nm side length on a glass substrate are covered with a layer of SU 8. As reported earlier,²⁰ the highest NFE of these structures when irradiated by a 795 nm fs pulse is along the polarization of the laser beam (see Figure 3, III). We will focus on the maximum NFE at the tip of the triangle along this polarization.

The experimental results for the maximum NFE of the nanotriangles have been determined according to eq 1 and are shown in Figure 4. The average NFE is 600 with a standard

Figure 4. Enhancement of the near field intensity (NFE) as a function of the fwhm of a Gaussian laser profile of 40 nm thick gold triangles with 85 nm side length for 50 mW (black) and 75 mW (red) incident laser power and varying irradiation time. The polarization of the laser beam is from base to tip.

deviation of 140, independent of the incident laser power, irradiation time and size of the Gaussian laser beam on the surface. The error bars represent the uncertainties in the position of the thresholds in polymerization.

In order to link the FDTD simulations and experimental results, the extinction spectra of the structures are compared (see Figure 5). The main resonance of the structures is at 740

Figure 5. Experimental and calculated extinction spectra of the 40 nm thick gold triangles with a side length of 85 nm. The oscillations in the experimental data originate from interferences due to the finite thickness (3 μm) of the SU 8 layer. The inset shows the calculated NFE of the structures (shown as the white triangle) 3 nm above the substrate for the polarization direction indicated by the arrow. In the simulations, an infinitely thick SU 8 layer was incorporated. The length of the scale bar is 100 nm.

± 100 nm in the experiment and 750 ± 50 nm in the FDTD simulations for the dipole mode of the triangle.²⁰ The modulation of the experimental resonance curve originates from interferences inside the 3 μm thin SU 8 layer. The NFE does not only depend on the lateral position, but also on the height above the substrate. Figure 6 (right panel) shows the simulated near field distribution at a distance of 3 nm above the substrate, where it achieves its highest value of 2600 at the tip of the structure. The variation perpendicular to the sample plane along the edge of the tip from the bottom to the top of the structure is shown in the left panel of Figure 6.

Figure 6. Dependence of the near field enhancement on the height above the substrate (left) and around the tip at a height of 3 nm (right). The insets show the results of the FDTD simulation at the tip of the triangle in a side view (left) and a top view (right). The profile is taken between the red markers, and the white dashed lines indicate the position of the gold triangle. The scale bar in both insets is 20 nm. The arrow in the right panel indicates the spatial resolution of the experiment that amounts to 25 nm limited by the detection of the smallest polymerized resin particles.

DISCUSSION

In order to obtain the value α of the NFE with the shown method, it is essential to identify the threshold for the polymerization in the area between the triangles and at their tips. Especially the latter part is challenging, as the smallest polymer structure that was observed has a diameter of 25 nm (Figure 3, II), smaller structures could not be identified with confidence. Thus, the actual NFE is supposed to be higher than reported here. Furthermore, the smallest polymerized structures may accidentally be removed when rinsing off the nonpolymerized resin, as the adhesion of the resin on the substrate is low. This leads to a systematic underestimation of the polymerization threshold. One advantage of our method is its inbuilt statistical information by averaging over a large array of at least 300 structures. The statistical variations are reflected in the error bars in Figure 4. The statistical error originates from size and shape variations of the individual triangles. These are partially caused by defects in the colloidal mask or subsequent processing steps. Therefore, we limited the statistical analysis to defect free triangles, that is, isolated triangles with three clearly visible tips. The quantitative determination of α is quite insensitive to potential errors in the determination of the exact position of the polymerization threshold at the tip as it is positioned in the very shallow region of the Gaussian laser profile. However, the uncertainty in the threshold without NFE plays a more important role, especially for small spot diameters, as the gradient of the Gaussian intensity distribution is steeper in this case.

The colloidal mask used for the fabrication of the nanostructures forms a two dimensional polycrystalline hexagonal lattice with a grain size of several micrometers consisting of spherical polystyrene particles with a diameter of 320 nm. The orientation of the lattice varies randomly from grain to grain. This distribution of orientations is reflected in the orientation of the arrays of the gold nanotriangles. This hampers the exact alignment of the polarization direction of the excitation with respect to the orientation of the triangles. However, FDTD simulations show that the triangular shape makes the maximum NFE at the tip quite insensitive to a variation in the angle of polarization. The NFE is only slightly decreased from 2600 to 2100 as the angle of polarization changes by 20 degrees out of the optimum axis, that is, perpendicular to the baseline of the triangle.

The spatial distributions of the NFE obtained by the FDTD simulation and by the experiment are in very good agreement. Nevertheless, the calculated maximum near field enhancement near the substrate is higher than the one measured by TPP. This discrepancy can be explained by (a) the resolution of the TPP and (b) by thermal cross linking of the SU 8. In Figure 6, the simulated lateral profile of the NFE at the tip and at the position of the maximum NFE is shown. For estimating the influence of possibility (a), we have to take into account that the maximum NFE obtained by FDTD is concentrated at a very small volume around the tip (Figure 6, right panel) and decreases from a NFE of 2600 to 600 for a distance of 5 nm in height (Figure 6, left panel). Laterally, it decreases from 2600 to 600 at 12 nm distance from the tip center. As described above, the smallest visible structure obtained by TPP is about 25 nm in width, resulting in a minimum resolution of the TPP in the same order. Thus, not the maximum NFE is measured, but the lowest NFE inside a minimal volume for polymerization. Possibility (b) considers that the high intensity generated at the tip might lead to a heating of the surrounding SU 8 and its cross linking at a lower intensity than the threshold intensity.²⁷ This effect should dominate for increasing irradiation time, as the heating of the SU 8 for a longer time will allow more cross linking due to an elevated temperature. The fact that in our experiment the NFE *does not depend* on the irradiation time, especially in the case of a spot size of 42.2 μm , shows that this thermal effect plays a minor role. One reason for this relatively small thermal effect is the good thermal contact of the SU 8 to the gold structure assuring fast heat transfer away from the tip. While the exact temperature increase is hard to estimate and thus its impact onto the determination of the NFE cannot be quantified, it is straightforward to understand that a thermal polymerization would result in an underestimation of the actual NFE: The minimal detectable size of the polymerized structures of 25 nm in our experiments is fixed. If local heating to a temperature above the polymerization temperature of SU 8 at the tips was present, this would result in bigger polymer structures at a given intensity and would thus be interpreted as a lower NFE by comparing with the theoretical data shown in Figure 6 (right panel). Summarizing, the combination of both effects, (a) and (b), leads to a *lower* measured NFE than theoretically achievable because of a bigger size of the polymerized structure than given by the calculated profile of the NFE at the edge of a nanostructure.

The experimentally and theoretically obtained values for the NFE are significantly higher than those reported by Sundaramurthy et al.³ This can be explained by the missing conductive adhesion layer in our case, which improves the near field enhancement of the nanostructure. A quantitative comparison with the results of Deeb et al.²⁰ is difficult, as the geometry and materials are different. However, it can be concluded that the much sharper structures in case of the nanotriangles, as compared to the spheres with 60 nm diameter used in ref 20, lead to the observed higher NFE.

From the systematic variation of our experimental parameters, we deduce a threshold fluence of $0.25 \pm 0.1 \text{ J/cm}^2$ for most of the spot sizes for an fs laser operating at a wavelength of 795 nm, 82 MHz repetition rate, and a 130 fs pulse length (see Supporting Information) in our experiments.

CONCLUSION

By irradiating metallic triangular shaped gold nanostructures covered with SU 8 with a Gaussian intensity profile and comparing the threshold for polymerization with and without the near field enhancement at the position of interest, we determined the maximum near field enhancement in case of a 40 nm thick gold triangle with 85 nm side length on a glass substrate to be 600 ± 140 , independent of the irradiation time and incident laser power. The smallest structures obtained with this method were 25 nm in diameter, setting the resolution limit of the method. FDTD calculations show a pointlike maximum NFE of 2600 with a fwhm of only 12 nm in the lateral and 5 nm in the vertical direction. Taking the finite lateral resolution into account, the simulation results are in agreement with a NFE of 600–800 as found in the experiments. Additionally we estimated the threshold fluence for polymerization of SU 8 to 0.25 J/cm^2 for a femtosecond laser with 82 MHz repetition rate.

Although in this experiment the nanostructures are partially placed in an environment with a higher refractive index than air, the combination with the analysis of the extinction spectra enables one to use the presented straightforward method to determine the near field enhancement. The comparison of the experimental results with those from theoretical methods like FDTD and DDA help to further improve these numerical methods.

EXPERIMENTAL SECTION

For the two photon polymerization (TPP), a laser with 130 fs pulse width and 795 nm wavelength is used. To test the independence of power and irradiation time, the power of the laser beam was chosen as 50 and 75 mW and the irradiation time between 4 and 100 s.

In the setup for TPP, the beam profile of the femtosecond laser is optimized by a pinhole and subsequently collimated with a single lens on a translation stage and directly interacts with the nanostructures without going through the substrate. The polarization of the laser beam is achieved by an additional polarizer in the setup. By moving the lens out of the optimum position, the beam changes its divergence slightly and the spot diameter on the substrate is increased. The obtained beam diameters on the substrate as a function of the position of the lens are shown in Figure 1. A slight tilt of the beam out of the optical axis of the objective lens ensures that the reflected light from the second surface of the substrate does not interact with the irradiated area. For the experiments, only the nontilted and by a factor of 1.05 shorter axis of the elliptical spot is used to obtain the near field enhancement of the nanostructures. The beam profile on a substrate is captured by a CCD camera mounted on an optical microscope and analyzed later by the software Gwyddion.

The nanostructures used in these experiments are fabricated by colloidal lithography²⁹ with polystyrene nanospheres of 320 nm in diameter from Interfacial Dynamics Corporation. Subsequent thermal evaporation of 40 nm gold produces triangular gold nanoprisms with a side length of 85 nm on a SiO_2 substrate. Strictly speaking, the nanostructures produced in this way are truncated triangular pyramids rather than prisms, because the holes in the colloid mask are gradually reduced in size as the metal is evaporated.³¹ For the present structures, this is a minor correction which is neglected here. After removal of the colloidal particles, the substrate is washed in methanol and cleaned in a plasma cleaner. Prior to spin coating the resin (SU 8 2002, Microchem. Co.), the substrate is baked for 1 min at 150 °C to remove water on the substrate and improve the adhesion of the 2.5 μm thick SU 8 layer. The thickness was calculated from the interference seen in Figure 5. After postbaking of the structures, development, and washing with 2 methoxy 1 methylethyl acetate and 2 propanol, the structures are sputtered with 2 nm tungsten and investigated by SEM. Also a part of the gold triangles is removed due to the weak adhesion of gold to SiO_2 , resulting locally in arrangements of only two triangles in a dumbbell like arrangement, as shown in Figure 3, III. Here, the distances of the threshold of polymerization from the center with and without near field enhancement are obtained by averaging over several structures, as inhomogeneity in the nanostructures and loss of polymerized structures have to be compensated. These variations in the determined distances lead to the error bars shown in Figure 4. Polymerization effects on nontriangular structures are omitted when determining the thresholds.

For the simulation of the near field enhancement and extinction spectra, the commercially available FDTD program by Lumerical Inc. has been used, building on previously reported studies.^{8,21} The simulated unit cell of the gold triangle array consists of a 40 nm thick gold structure with rounded edges (curvature radius at the tip in the order of 5 nm) on top of a bulk SiO_2 substrate, as reported in our earlier publication.²¹ We have used a 1.5 nm mesh size with periodic boundary conditions and the material data from Palik and Ghosh,³² and a refractive index of 1.56 for SU 8.³³ For comparison with the structures used in the FDTD simulations (Figures 5 and 6), a nanotriangle used in the experiment can be seen in Figure 3, II.

ASSOCIATED CONTENT

Supporting Information

Determination of the threshold for polymerization. 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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