Nanoscale

Highly efficient plasmonic tip design for plasmon nanofocusing in near-field optical microscopy

Takayuki Umakoshi, Yuika Saito and Prabhat Verma*

Near-field scanning optical microscopy (NSOM) combined with plasmon nanofocusing is a powerful nano-analytical tool due to its attractive feature of efficient background suppression as well as light energy compression to the nanoscale. In plasmon nanofocusing-based NSOM, the metallic tip plays an important role in inducing plasmon nanofocusing. It is, however, very challenging to control plasmonic properties of tips for plasmon nanofocusing with existing tip fabrication methods, even though the plasmonic properties need to be adjusted to experimental environments such as the sample or excitation wavelength. In this study, we propose an efficient tip design and fabrication which enable one to actively control plasmonic properties for efficient plasmon nanofocusing. Because our method offers flexibility in the material and structure of tips, one can easily modify the plasmonic properties depending on the requirements. Importantly, through optimization of the plasmonic properties, we achieve almost 100% reproducibility in plasmon nanofocusing in our experiments. This new approach of tip fabrication makes plasmon nanofocusing-based NSOM practical and reliable, and opens doors for many scientists working in related fields.

1. Introduction

Nanofocusing of a light field through a plasmon has received increased attention because of its attractive feature of compressing light energy into a nanometric volume. Until now, many efforts have been made not only for scientific studies of plasmon sensing,1–7 but also for various applications, such as optical sensing,8 optical signal control,9,10 nano-lithography and optical nano-circuits.11 In particular, near-field scanning optical microscopy (NSOM) with plasmon nanofocusing has recently emerged as a great combination that enhances the performance of NSOM, not just because of light energy compression to the nanoscale but also because of the drastic suppression of background scattering.12–15 NSOM offers nanoscale spatial resolution as well as abundant information through optical analysis via near-field light excited at the apex of a metallic tip.16–23 In ordinary NSOM, however, one is forced to illuminate the tip apex with an incident far-field laser to excite near-field light at the tip apex, and as a result, one always suffers from huge background scattering by the incident laser, which has been a key issue in NSOM for a long time.

In the case of plasmon nanofocusing, on the other hand, the tip is illuminated far from the apex to generate near-field light through plasmon excitation that compresses and propagates to the apex. This means that there is no need to illuminate the apex directly. Therefore, there is no concern about background scattering by far-field laser illumination, which leads to much better sensitivity in NSOM. It should be noted that the plasmon nanofocusing technique has completely different characteristics to existing noise reduction methods such as modulation techniques24,25 or far-field subtraction26 in terms of the fact that plasmon nanofocusing ideally does not have any background scattering, whereas the other methods reduce the existing background scattering. Since Raschke et al. demonstrated plasmon nanofocusing on a metallic tip in 2007,27 an increasing number of reports about NSOM using plasmon nanofocusing have been published, e.g., in optical nano-imaging12,28,29 and nano-Raman analysis.13,30

In these studies, as one can expect, the metallic tip plays a very important role in plasmon nanofocusing. Thus far, there is only one tip fabrication method that has been proposed and often discussed, which is electrochemical etching.10,27,31 This method produces a fully metallic tip by pulling a metallic wire in chemical solution.19 One of crucial issues in this method is that the shape and material of tips are limited, which are mostly gold tips in a conical shape. This fact has restricted the versatility of plasmon nanofocusing-based NSOM because it is not possible to adjust the plasmonic properties of tips for efficient plasmon nanofocusing, depending on experimental requirements such as excitation wavelength and sample. Therefore, a tip fabrication method that offers flexible control of plasmonic properties is highly required.
In this work, we propose an efficient design of plasmonic tips for plasmon nanofocusing, which offers multiple parameters for the flexible, active and precise control of tip plasmonic properties. We believe that our tip fabrication method will lead to practical plasmon nanofocusing-based NSOM adjustable to arbitrary experimental conditions. We also report that, due to the optimization of the plasmonic properties plasmon nanofocusing is highly efficient, such that our method achieved almost 100% reproducibility in plasmon nanofocusing on fabricated tips, which is an important development in plasmon nanofocusing-based NSOM to further make this technique practical and reliable. Our tip design is composed of a dielectric body structure in a pyramidal shape and a metallic thin layer on one surface of the body structure, as shown in Fig. 1(a). It has a grating structure on the metallic thin layer that works as a plasmon coupler. Plasmon nanofocusing is induced on the tapered metallic layer by illuminating the grating with a laser to generate near-field light at the apex. We have also developed a technique to easily deposit an extremely smooth metallic layer on one surface of the tip-body via thermal evaporation, which allows one to have various options for the material of the metallic thin layer such as gold, silver, copper and aluminum, each of which shows very different plasmonic properties, covering a wide range of plasmonic frequencies ranging from the ultraviolet to the infrared regions. In addition to the metallic thin layer, we can also select a dielectric material for the body of the tip from various materials available, such as silicon, silicon nitride, diamond, boron-doped diamond, etc., which also control plasmon behavior through their dielectric constants. Besides, oxidation of the body material also allows to control the dielectric constant of the material, which provides vast variety of materials that one can use as body material. Since the plasmon propagation mode on the tip strongly relies on both the metallic and dielectric materials, it will greatly broaden the frequency range of plasmon nanofocusing with high efficiency. Thickness of the metal layer is also an important parameter to control the plasmon propagation mode because it affects the interaction of plasmons on both sides of the metallic thin layer. The thermal evaporation technique allows precise control of the thickness, which means that further optimization of the plasmon propagation mode is possible after choosing two materials, one metal and one dielectric. In our experiment, by carefully choosing materials and optimizing the thickness of the metal, we evaluated the best conditions for plasmon nanofocusing for a particular excitation wavelength used in our experiments so that we could achieve high reproducibility of inducing plasmon nanofocusing. Finite-difference time-domain (FDTD) simulation confirms that our tip design efficiently induces plasmon nanofocusing and generates strong near-field light at the apex, as seen in Fig. 1(b), where silver (thickness = 40 nm) and silicon dioxide were used as the metallic thin layer and the tip body, respectively, and the excitation wavelength was 642 nm.

In addition, there are a few advantages associated with our tip design. Due to the flatness of the metallic coating, one can easily apply well-established nano-lithographic techniques, such as electron beam lithography or focused ion beam (FIB) lithography, without losing beam focus in contrast to the case of three-dimensional structures like electrochemically etched conical tips. It allows one to fabricate perfect structures as a plasmon coupler or any other plasmonic elements to modify the plasmonic properties of tips. Also, the metallic thin coating, which is deposited on only one side of the tip body, gives better efficiency compared to a fully metallic tip, because the direction of plasmon propagation is strictly restricted to the metal on one side and the near-field light propagates only towards the tip apex, resulting in efficient energy compression into the apex.

Fig. 1(c) shows a scanning electron microscopy (SEM) image of a fabricated tip, where a silicon dioxide cantilever tip was utilized as the body material. The inset shows an enlarged image of the tip, which is coated with a very smooth silver layer and has a grating structure away from the apex. It is
noted that our fabricated tips are based on commercially available silicon cantilever tips, which can be easily operated by any atomic force microscopy (AFM) system that uses an optical lever feedback technique, which is one of the most common NSOM configurations.\textsuperscript{18,41,42} Since electrochemically etched tips can only be used in tuning fork configuration or scanning tunnelling microscopy, this fact provides good opportunities for scientists working with optical lever feedback AFM. We would like to note that all of the advantages mentioned above cannot be achieved by conventional tip fabrication methods, and we expect the unique properties of our tip fabrication method to benefit scientific studies as well as applications in research related to plasmon nanofocusing.

2. Results and discussion
2.1 Fabrication of a cantilever-based metallic tip for plasmon nanofocusing

In this study, we optimized tip parameters for an incident laser wavelength of 642 nm, as this is one of the common wavelengths used in spectroscopic research. By optimizing our FDTD simulation results, we conclude that the best metal for the plasmonic thin layer is silver. The optimized thickness of the silver layer was estimated to be 40 nm for the best results. For a comparison, we found that gold thin layer resulted in about a 5000 times weaker near-field intensity at $\lambda = 642$ nm than that of silver. This is mostly because gold has a higher attenuation for plasmon propagation at this wavelength. Further, we examined several materials for the tip body and found silicon dioxide to be the best for this wavelength. As an example, our simulation showed that the near-field intensity was reduced by about 100 times, when we considered silicon as the tip body material, which is the most common material used in AFM cantilever tips. This leads us to an interesting conclusion that the choice of the material of the tip-body also plays an important role in efficient plasmon nanofocusing. Through this study, it is confirmed that the optimization of materials is essential, because a small difference in the optical properties of the materials used in tip fabrication may eventually create a huge difference in plasmon nanofocusing. Owing to our FDTD results, we decided to oxidize silicon tips to convert them into silicon dioxide, and to evaporate 40 nm thick silver layers on them to obtain the best plasmonic tips for efficient plasmon nanofocusing. Fig. 2(a) shows the procedure for tip fabrication. We first oxidized a silicon cantilever (NT-MDT/CSG-01) at 1000 °C in the presence of flowing water vapor in an electric furnace for 20 minutes, which turned silicon into silicon dioxide for the entire tip.\textsuperscript{37} We then deposited a smooth silver coating via thermal evaporation. The evaporation conditions are described below in detail. Lastly, we fabricated a grating structure using FIB lithography at a distance of about 8 µm away from the tip apex that works as a plasmon coupler. The height of the cantilever tips we used was around 15 µm, which was long enough to fabricate the grating far from the apex to prevent overlap between the incident laser
and apex. The grating period was also pre-optimized though FDTD simulation and was found to be 780 nm for the best coupling efficiency at $\lambda = 642$ nm.

For plasmon nanofocusing, the surface roughness of the metal film is an important factor as a smoother surface can drastically reduce the energy loss during plasmon propagation. In order to deposit a smooth surface, there are a few key points to note during the metal evaporation. One of them is the evaporation direction. For plasmonic tips used in ordinary NSOM, the metal is usually evaporated along the tip axis, which is at a low angle with respect to the tip surface. Once silver nucleus islands are deposited with low-angle evaporation, they create a shadow behind them, and no silver would later be deposited in the shadowed areas, resulting in a rough surface with silver grains, which is actually preferable for localized plasmon resonance.\textsuperscript{38,43–45} In contrast, for plasmon nanofocusing, the evaporation direction normal to the tip surface (high angle evaporation) results in a much smoother surface, because for a high-angle deposition, there is no such shadow effect. Fig. 2(b) shows surface roughness dependence on evaporation direction, calculated from root mean square (RMS) values. We have deposited 40 nm thick silver on silicon dioxide substrates at various evaporation directions, and measured the roughness by tapping-mode AFM. As one can see, the smoothest film was deposited in the case of the evaporation direction being perpendicular to the tip surface, which would result in a very low energy loss of plasmon propagation and thereby efficient plasmon nanofocusing.

Another key parameter that affects surface roughness of the deposited metal film is the evaporation rate. The evaporation process usually deposits silver in a granular structure, where the size of the grains and the average surface roughness across these grains depend upon the evaporation rate. Fig. 2(c) shows roughness dependence, which is calculated by the average RMS value obtained from the topography, on evaporation rate. We found that the roughness reduces as the evaporation rate increases. An average roughness of about 0.5 nm was achieved at an evaporation rate of 3 nm s$^{-1}$. Further, we observed that the grain size also increased with increasing evaporation rate. Fig. 2(d) shows SEM images of silver thin coatings evaporated at 0.04 nm s$^{-1}$ (upper half) and 3 nm s$^{-1}$ (lower half). For the faster evaporation rate of 3 nm s$^{-1}$, larger grains (several hundred nm) with very flat surfaces were achieved, whereas for a slower deposition rate of 0.04 nm s$^{-1}$, very small grains (10–20 nm) were obtained and no larger flat area could be observed. We assume that this is because the high kinetic energy of silver atoms causes silver vapor to diffuse around the surface and contributes to the growth process rather than the creation of another grain.\textsuperscript{46} Fig. 2(e) shows the topographic line profiles of a large grain (red curve) and the aggregates of small grains (black curve), for the deposition rates of 3 and 0.04 nm s$^{-1}$, respectively. The topographic line profiles show that the surface roughness remained within 0.5 nm on the surface of a large grain for the deposition rate of 3 nm s$^{-1}$, whereas it was several nanometers for the aggregated area of small grains for the deposition rate of 0.04 nm s$^{-1}$. Aggregates of small grains lead to a significant loss during plasmon propagation and are therefore not suitable for plasmon nanofocusing. These results clearly show that faster deposition that creates larger grains with smoother surfaces are preferred, as they are expected to contribute positively to efficient plasmon propagation with a low energy loss. In practice, there is a trade-off between roughness and accuracy of thickness control, and we optimally chose around 1.5 nm s$^{-1}$ as the evaporation rate in tip fabrication, in order to make the silver coating smooth enough together with an acceptable thickness control. With proper optimization, we obtained an averaged roughness of less than 1 nm. We have also investigated the surface roughness dependence on ambient pressure during evaporation, and have found that there is no strong dependence on the pressure if it is lower than $1 \times 10^{-4}$ Pa, because most dust particles that may affect silver deposition are removed at such a low pressure.\textsuperscript{46} We therefore used a pressure of around $5 \times 10^{-7}$ Pa in our experiments. This optimization of the surface roughness also contributes to the high reproducibility of our method.

Fig. 2(f)–(h) show SEM images of a tip at different fabrication steps. Fig. 2(f) shows a silicon dioxide tip. We confirmed that there are no changes in the tip shape during the oxidation process. Fig. 2(g) shows the oxidized tip with an extremely smooth silver thin layer. When we magnified the image, we observed large grains deposited on the tip surface as seen in the inset. At last, we fabricated a grating structure on the silver layer by FIB milling (Fig. 2(h)). Since the grating period is 780 nm, it does not require very high fabrication resolution. It is, therefore, easy and highly reproducible to fabricate the grating with an ordinary FIB lithographic technique.

### 2.2 Demonstration of plasmon nanofocusing on fabricated tips

We confirmed through optical measurements that the fabricated tips were able to produce plasmon nanofocusing. Fig. 3 (a) shows an optical image of a fabricated tip with laser illumination ($\lambda = 642$ nm) at the grating, where white dotted lines represent the outer shape of the tip and white arrows indicate incident polarization. We observed that a bright spot appears at the apex. The inset shows a magnified image of the bright spot at the apex. The incident polarization was perpendicular to the grating grooves. In order to confirm if the bright spot appeared because of plasmon nanofocusing, we investigated its dependence on incident polarization. At 45° of incident polarization angle with respect to the grating grooves, we observed a reduced intensity at the tip apex (Fig. 3(b)), and light spot disappeared at the apex when the incident polarization was parallel to the grating grooves (Fig. 3(c)). In a thorough investigation of incident polarization, as shown in Fig. 3(d), we obtained a dipole-like intensity variation, which suggests that the bright spot is caused by far-field emission from near-field light generated through plasmon nanofocusing.\textsuperscript{12} Here, 0° corresponds to parallel polarization, and 90° corresponds to normal polarization. To further confirm this, we performed an FDTD simulation, which is shown by the
green line in Fig. 3(d). The simulation results are in good agreement with our experimental results.

We would like to note again that our fabrication method provides efficient plasmon nanofocusing through optimization of the tip material and geometry, especially of the thickness and the surface roughness, so that we observe plasmon nanofocusing in almost 100% of the fabricated tips for a sample of more than 50 fabricated tips. In order to emphasize the reproducibility of our experiments, we show some optical images of different fabricated tips in Fig. 4, where the laser is illuminated at the gratings. All tips show bright spots at their apexes, which are distinctly spatially separated from the laser illumination.

2.3 Near-field imaging with plasmon nanofocusing

In order to emphasize the plasmonic properties of our fabricated tips, we demonstrated near-field imaging with plasmon nanofocusing. In these experiments, Rayleigh scattering from the sample was detected to evaluate tip performance. Fig. 5(a) illustrates the experimental setup for near-field measurement. An incident laser (CW, \( \lambda = 642 \) nm) was focused on the grating of our fabricated tip through a single-mode optical fiber and an objective lens (NA = 0.28, WD = 30 mm, \( \times 20 \)). Incident polarization was controlled by a polarizer right before the objective. Illumination position was controlled by an actuator in the \( x-y-z \) directions. Near-field light was then created through plasmon nanofocusing (see the illustration in the lower left inset), and the Rayleigh scattered signal from the sample was collected through another objective (NA = 1.4, \( \times 60 \)).
at the bottom. We utilized a pinhole (30 µm) and a spatial mask to block scattered light from the grating. Working as a confocal element, the pinhole efficiently extracts a signal from the vicinity of the tip apex. The spatial mask allows only high NA components to pass, whereas the scattering at the grating, which exists at low NA, is blocked by the mask (see the inset). This configuration perfectly blocks Rayleigh scattering from the grating, and near-field scattering from the tip apex is measured. Finally, the signal was detected by a liquid-nitrogen-cooled CCD camera.

Here, we chose carbon nanotubes (CNTs) as a standard sample. CNT powder (NanoIntegris, IsoNanotubes-M) was sonicated for about 30 minutes in a solution of 1,2-dichloroethane, and then the solution was dropped and spin-coated on a cleaned cover slip.47 The CNT sample was synchronously scanned using a piezo stage under AFM control together with near-field signal detection. Fig. 5(b) shows an AFM image of the CNT sample. Fig. 5(c) shows a Rayleigh-scattered near-field optical image of the same area, measured with plasmon nanofocusing. We observed strong scattering from the sample, where a dramatic contrast can be seen at different locations of CNTs. Please note that no modulation technique or far-field subtraction was applied for background suppression. We clearly observed a background-free near-field image of the CNT sample owing to the plasmon nanofocusing. We examined the intensity line-profile along the white dotted lines in Fig. 5(c), and obtained a spatial resolution of 30 nm, far beyond the diffraction limit. At the same time, we did not see any image contrast in the case where the polarization was parallel to the grating (Fig. 5(d)), which again proves successful plasmon nanofocusing. We confirmed that our fabricated tips were evidently reliable for near-field microscopy.

3. Conclusions

In conclusion, we propose a tip design that enables one to control the plasmonic properties of tips for efficient plasmon nanofocusing, where the tip is composed of a metallic thin layer and a dielectric pyramidal body structure. Since our fabrication method provides control of multiple parameters that can affect plasmonic properties, it allows us to flexibly control the plasmonic properties of tips to meet experimental requirements, such as the incident laser, the sample and so on, which has not been possible with conventional tip fabrication methods. In our experiments, we optimized the plasmonic properties for a 642 nm excitation wavelength, where silver and silicon dioxide were used, and the thickness and the surface roughness of silver coating were optimized to 40 nm and below 1 nm, respectively, resulting in almost 100% reproducibility of plasmon nanofocusing, as demonstrated through optical measurements. The high reproducibility is a much appreciated development to make plasmon nanofocusing-based NSOM measurements reliable. We confirmed through polarization investigation that the light spot observed at the tip apex was actually produced through plasmon nanofocusing. At this moment, although we focused on a certain incident wavelength of 642 nm, the frequency range can be much broadened from ultraviolet to infrared through further optimization. In addition, we would like to note that our fabricated tip is based on cantilevers, which allows it to be easily applied to conventional AFM systems that use optical lever feedback, and provides good opportunities for scientists working with AFM. We have also shown that our fabricated tips are reliable for NSOM measurements, by conducting near-field imaging of CNTs with plasmon nanofocusing at nanoscale spatial resolution. Importantly, we clearly observed a background-free image of CNTs without a modulation technique or other noise-reduction techniques. We expect that our reproducible and reliable cantilever-based tips will lead to further development in research related to this field.

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References

13 F. D. Angelis, G. Das, P. Candeloro, M. Patrini, M. Galli, A. Bek, M. Lazzarino, I. Maksymov, C. Liberale,