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## Fabrication of Near-Field Plasmonic Tip by Photoreduction for Strong Enhancement in Tip-Enhanced Raman Spectroscopy

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Tip-enhanced Raman spectroscopy (TERS) offers one of the best techniques for optical analysis and imaging of samples at nanoscale. The most important point in TERS experiments is to obtain a high signal enhancement through a metallic nanotip. Compared with fully metallized tips, the tips that have only one metallic nanoparticle at the apex show better enhancement. Here, we demonstrate a new and simple way to fabricate metallic nanoparticles selectively at the tip apex through photoreduction. By controlling the nanoparticle size, the plasmon resonance of the tip can be tuned. Finally, we demonstrate that such tips give better enhancement in TERS. © 2012 The Japan Society of Applied Physics

Tip-enhanced Raman spectroscopy (TERS) has matured over the years establishing itself as a promising tool for analyzing and imaging samples at true nanoscales spatial resolution far beyond the diffraction limits of the probing light.<sup>1,2</sup> TERS utilizes a metallic nanotip that acts as a plasmonic antenna to enhance the originally weak Raman scattering from a nanometric volume of a sample.<sup>1–5</sup> One of the most common techniques for fabricating metallic tips for TERS is coating a thin metallic layer on a semi-conducting cantilever tip through vacuum vapor deposition.<sup>6–9</sup> Such tips can be controlled using an atomic force microscopy (AFM) controller, providing an easy way to scan the tip during TERS imaging. Some researchers, however, prefer to use solid metal nanotips, such as the ones used in scanning tunneling microscopy. In both cases, the length of the metal along the axis of the tip is on the order of a few to a few tens of micrometers, which is much larger than the wavelength of the visible light used in TERS. The localized surface plasmon polaritons (SPPs) thus find a longer path along the tip axis, and the resultant plasmon frequency of the tip is red shifted with increasing length of the metallic tip.<sup>10</sup> We also confirmed through a simple finite-difference time-domain (FDTD) simulation that the longer tips have their plasmon resonances shifted out of the visible range. Thus, if the size of the metal on a nanotip is limited to a certain length, it would give better enhancement in the visible range compared with fully metallized tips.

There has already been some interest in partially metallized tips, and some researchers have predicted stronger enhancement through numerical analysis.<sup>11,12</sup> Others have tried to fabricate such tips either by attaching a metal nanoparticle on the tip apex by glue using an AFM controller or by fabricating a nanoparticle on a tip apex using focused ion beam (FIB) lithography.<sup>13–17</sup> Both methods need complicated experimental setups such as AFM or FIB systems, result in poor reproducibility, and need a long fabrication time. At present, there are no established practical methods for the fabrication of near-field tips with a small metallic nanoparticle at the apex, which could be highly reproducible, simple, and quick. A facile fabrication method is essential to fully explore the potentials of TERS analysis and imaging.

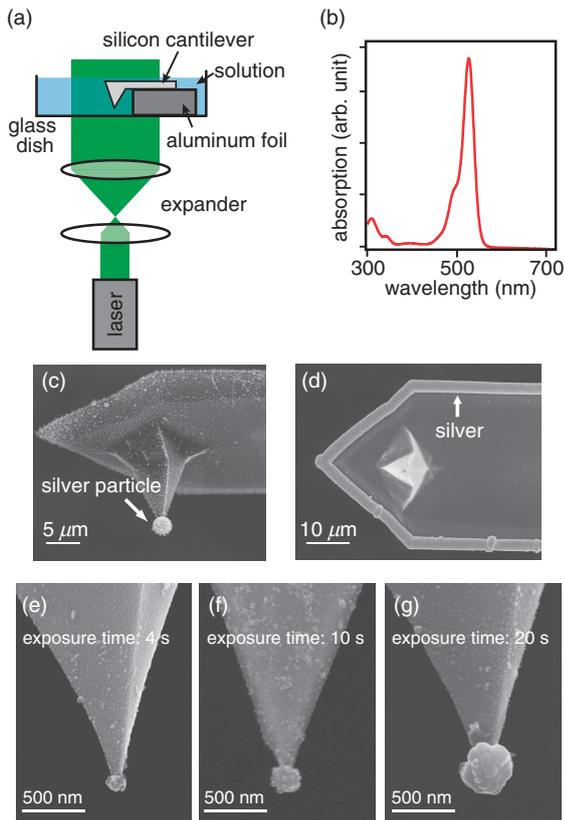
In this study, we present photoreduction as a facile method of fabricating a silver nanoparticle at the tip apex.

Our technique is very simple, highly reproducible, and can be used to fabricate a tip within a fraction of a minute. We found a particular property of photoreduction that it occurs selectively at sharp corners, such as the tip apex of a silicon cantilever, even if the cantilever is irradiated entirely. By taking advantage of this property, we succeeded in growing silver nanoparticles selectively at the tip apex. One of the vital advantages of the photoreduction technique is that the size of metal nanostructures grown at the apex of the tip can be well controlled by optimizing various parameters in the experiment.<sup>18</sup> We can thus choose a nanoparticle size that suits better for strong plasmon resonance for a desired laser wavelength. Furthermore, we demonstrate that we can successfully perform TERS measurements using our fabricated tip, which showed about an order of magnitude higher enhancement of Raman scattering intensity compared with a tip that was fully coated with silver via vacuum vapor deposition.

Figure 1(a) shows the experimental setup used to fabricate the silver nanoparticle at the tip apex by photoreduction, which does not require any complicated equipment. Commercially available AFM silicon cantilevers were used as the tips in our experiments. As seen from Fig. 1(a), the cantilever tips were placed in a glass dish facing downwards and an aluminum foil (thickness: 24 μm) was used as a spacer so that any physical contact between the dish and the tip apex could be avoided even after the growth of the silver nanoparticle. A small amount of solution containing eosin-Y-disodium (eosin), *N*-methyldiethanolamine (MDEA), AgNO<sub>3</sub>, and water was dropped in the glass dish. The entire cantilever was then irradiated from the bottom with an unfocused and expanded beam of a yttrium aluminum garnet (YAG) laser ( $\lambda = 532$  nm). Figure 1(b) shows the absorption spectrum of the solution containing eosin and MDEA, confirming that the solution has strong absorption for the laser used here. Eosin behaves as a photoinitiator for the reduction reaction of Ag<sup>+</sup> by absorbing light. Under the laser irradiation, eosin changes MDEA into  $\alpha$ -aminoalkyl radical, which has reduction ability. Then, the  $\alpha$ -aminoalkyl radical efficiently converts Ag<sup>+</sup> to Ag atom, and finally, Ag atoms grow to form silver nanoparticles (AgNPs).<sup>19</sup> The tip was then washed with clean water, and it was ready to use.

Figures 1(c) and 1(d) show scanning electron microscopy (SEM) images of a tip apex and edges of a silicon cantilever, respectively, after photoreduction. Interestingly, Ag was selectively deposited at the tip apex and edges of the

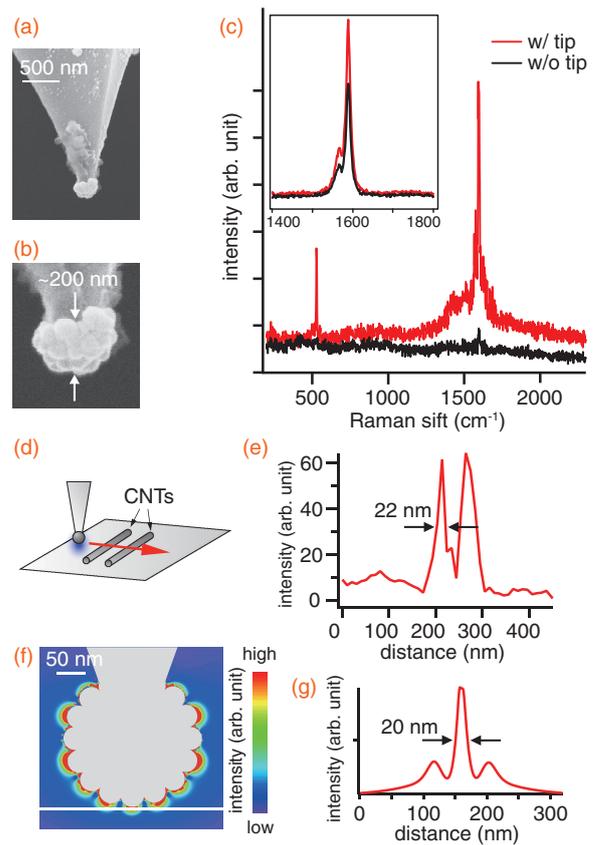
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**Fig. 1.** (a) Experimental setup for the fabrication of near-field tips by photoreduction. (b) Absorption spectrum of solution that contains eosin ( $1 \times 10^{-5}$  mol/L) and MDEA ( $1 \times 10^{-2}$  mol/L), showing the absorption peak at around 532 nm. (c) SEM image of an AFM cantilever tip after photoreduction. A silver nanoparticle is selectively fabricated at the tip apex. Selective growth is also observed at the edges of the cantilever in (d). (e)–(g) SEM images of tips after photoreduction with different laser exposure times indicated in the figure. The size of AgNPs increases from 100 to 400 nm with the exposure time. Laser power-density used in these experiments was  $10 \text{ mW/cm}^2$ . The concentrations of chemicals used here were  $1 \times 10^{-3}$  (eosin), 1 (MDEA), and  $5 \times 10^{-2}$  mol/L ( $\text{AgNO}_3$ ).

cantilever, which represent sharp corners of the cantilever. There are two possible reasons for this peculiar phenomenon. One is the lightning rod effect, where the light field is enhanced near the sharp corners of the cantilever.<sup>20</sup> Due to the increased value of the light field at sharp corners, the process of photoreduction starts near these corners, resulting in the selective growth near the corners. The other possible reason is the difference in the surface energy of silicon cantilevers between the flat surface and sharp corners. The nucleation energy of silver strongly depends on the surface energy of the substrate. A high surface energy gives a low nucleation energy. Since the nucleation is the highest energy barrier in the growth process of silver, the decrease of the nucleation energy means a faster selective growth of silver at higher surface energy regions.<sup>21,22</sup> Thus, this mechanism could be the other explanation for the selective growth of silver at the sharp edges, as seen in Figs. 1(c) and 1(d).

The result shown in Fig. 1(c) was obtained to demonstrate the phenomenon of selective growth at the corners. However, the AgNP grown here was larger than our goal. After optimizing the experimental parameters properly, we could easily control the size of the grown AgNP, as seen in Figs. 1(e)–1(g). The sizes of the grown AgNPs were 100,



**Fig. 2.** (a) SEM image of a tip fabricated by photoreduction, which we utilized for TERS measurements. (b) Zoomed SEM image of (a). (c) TERS spectra of CNTs taken using the fabricated tip. Inset shows TERS spectra taken using a standard tip that was fully coated with silver. (d) Illustration of experimental configuration for TERS measurement with scanning on two aligned CNTs. (e) TERS intensity at G-band with respect to the tip position for a one-dimensional tip scanning shown in (d). (f) FDTD simulation of field distribution in the vicinity of a model tip having a similar shape as the actual tip shown in (b). (g) Line profile of field intensity along the white line shown in (f).

200, and 400 nm for exposure times of 4, 10, and 20 s, respectively, in Figs. 1(e), 1(f), and 1(g). Here, we note that AgNPs were fabricated with the short exposure of several seconds; thus, the entire experiment for the fabrication of the tip could be finished within a few minutes.

Finally, in order to demonstrate the plasmonic properties of our tips fabricated by photoreduction, we performed TERS measurements by employing our tips and confirmed their plasmonic qualities by evaluating the enhancement factors in TERS. The experimental setup that we established for TERS measurement is described elsewhere.<sup>1,6</sup> We selected one of the fabricated tips, which was controlled using the contact-mode AFM system, for scanning. Raman spectra were measured in backscattering geometry using an objective lens with a high numerical aperture ( $\text{NA} = 1.4$ ) and an Ar-ion laser (wavelength: 488 nm). The tip used in this experiment, shown in Figs. 2(a) and 2(b), had a AgNP whose length along the tip axis was around 200 nm. Since carbon nanotubes (CNTs) are one of the best samples for judging the enhancement in TERS, we utilized CNTs as the sample in our experiments.

Figure 2(c) shows the obtained tip-enhanced Raman spectra of CNTs in the G-band spectral range. When our

fabricated tip approached the sample, we observed a strong enhancement of Raman scattering (upper spectrum) in comparison with the case when the tip was away from the sample (lower spectrum). In order to assess this enhancement with respect to the standard enhancement in TERS, we also measured the same sample with a standard tip that was fully coated with silver. The results are shown in the inset of Fig. 2(c). Just for the sake of precaution, we utilized ten times lower laser power when we measured Raman spectra with our tip fabricated by photoreduction. Therefore, these spectra look slightly noisy in comparison to the spectra in the inset. However, this does not affect the value of enhancement factor. As can be seen from the raw data, our fabricated tip obviously enhanced Raman scattering more than the fully metallized tip. Furthermore, in order to understand the spatial resolution of our tip, we chose a sample area where two isolated CNTs were lying parallel, and then scanned the tip along a line perpendicular to the CNTs while measuring the Raman intensity at the G-band, as illustrated schematically in Fig. 2(d). The resultant G-band Raman intensity at  $1590\text{ cm}^{-1}$  with respect to the position of the tip is shown in Fig. 2(e), which actually represents a one-dimensional TERS image of the sample. As indicated in the figure, a spatial resolution of 22 nm was obtained, which is remarkably beyond the diffraction limit. Interestingly, the spatial resolution is much better than the size of the AgNP grown at the tip apex. This high resolution was obtained due to the fact that the AgNP at the tip apex is not in the shape of a perfect sphere. Rather, it has a roughness due to aggregated silver grains of 20 nm size, as can be seen in the enlarged SEM image in Fig. 2(b). These aggregated silver grains could be responsible for the strong local confinement of light within a volume comparable to the grain size. In order to confirm our claim, we investigated the influence of roughness on the distribution of the enhanced field by FDTD simulation. As the model of the simulation, a AgNP of 200 nm diameter with surface roughness of 20 nm was designed. Figure 2(f) shows the structure of the model tip as well as the field distribution calculated by FDTD simulation. Figure 2(g) shows a line profile of field intensity near the tip apex [along the white line indicated in Fig. 2(f)]. The full width at half maximum of the field intensity right under the tip apex was 20 nm, which is close to the spatial resolution we obtained in the experiment. This explains how we could obtain a spatial resolution much better than the overall size of the AgNP. Indeed, as we examined our other tips, the formation of aggregated silver grains is a common feature of the tips grown by photoreduction, which allows us to obtain a high spatial resolution.

After confirming the spatial resolution for our fabricated tip, we estimated the enhancement factor (EF) of Raman scattering intensity in Fig. 2(c). The value of EF is usually estimated from the ratio of intensity per unit volume between the near-field and far-field measurements. By assuming the near-field light confined to 22 nm and the far-field light confined to 420 nm (obtained from the size of the focal spot), we calculated the EF at the G-band

( $1590\text{ cm}^{-1}$ ) to be  $4.8 \times 10^4$ . At the same time, EF obtained for the standard tip was  $2.7 \times 10^3$ , which was calculated from spectra in the inset of Fig. 2(c), which is about 20 times smaller than that of our fabricated tip. The value of EF obtained for the standard tip is similar to the values reported in the literature.<sup>1,6,9</sup> Thus, we can confidently say that the enhancement obtained with our tip fabricated by photoreduction is at least an order of magnitude larger than the values obtained with fully metallized tips.

In conclusion, we presented photoreduction as a facile fabrication method for growing near-field tips having only one silver nanoparticle at the tip apex. Our technique that selectively grows a silver nanoparticle at the tip apex involves just a simple laser radiation without any requirement of complicated techniques and experimental systems, and the entire fabrication process can be completed in a very short time (a few minutes). It is very easy to control the size of the fabricated silver nanoparticle to meet the TERS experimental requirements. Most importantly, these tips grown by our method provide an order of magnitude higher enhancement in comparison with the fully metallized standard tips. Our technique of growing tips with a silver nanoparticle has a possibility of improving TERS to a level where it could be a more practical and powerful nanospectroscopic tool due to the better enhancement of the weak Raman signal.

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