Fabrication of Silver Probes for Localized Plasmon Excitation in Near-field Raman Spectroscopy

Yuika Saito,[†] Takashi Murakami,[†] Yasushi Inouye,[*,†,††] and Satoshi Kawata[†,†††]
[†]*RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako 351-0198*
[††]*Graduate School of Frontier Biosciences, Osaka University, 2-1 Yamadaoka, Suita 565-0871*
[†††]*Department of Applied Physics, Osaka University, 2-1 Yamadaoka, Suita 565-0871*

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We present a new method for preparing a silver probe for tip-enhanced near-field Raman spectroscopy. In this method, the probe is coated with silver colloids by a simple chemical reaction known as a *mirror reaction*. Silver particles $\approx$40 nm in diameter, which is ideal for localized surface plasmon excitation in the visible wavelength range, are formed at the tip apex with high reproducibility. Futhermore, tip-enhanced Raman spectra of single-walled carbon nanotubes were measured by using the probe.

Tip-enhanced Raman spectroscopy (TERS) is a powerful tool in obtaining nanoscale information about molecules.[1–7] With this technique, the very weak signal detected by Raman scattering from a small number of molecules can be significantly enhanced by coating the probe tip with noble metals such as silver or gold to increase the scattering cross section by generating local surface plasmons. Since the spatial resolution and sensitivity of near-field Raman experiments strongly depend on the performance of the metal coated probe, the development of a near-field probe exhibiting strong and stable enhancement, as well as good spatial resolution, is a necessity. Silver colloids are ideal for local surface plasmon generation since the imaginary part of the dielectric constant in silver is quite small and their absorption lies in the visible wavelength range.[8] An ideal silver surface for surface-enhanced Raman spectroscopy (SERS) is a stable, well-packed film of silver particles whose particle size can be readily controlled at around 40 nm.[8,9] Achieving this control, however, is not straightforward, and consequently, a great deal of effort has been invested in developing metal films for surface plasmon applications in recent years. Several methods have been used, including (1) vacuum evaporation and sputtering, which is the most common method,[10,11] (2) electrochemical roughening,[12,13] and (3) the direct attachment of nanoparticles using functionalized surfaces.[14,15]

In this paper, we present a new method of coating a near-field probe with spherical silver particles whose size is controlled, for localized plasmon excitations. These probes were also evaluated by measuring tip-enhanced Raman spectra.

The *mirror reaction* method is an electroless plating technique that forms a silver surface of well-packed particles on various kinds of substrates, such as glass, silicon, silicon nitride, mica, and polymers. The optimal coating conditions such as temperatures, concentrations, and reaction times are different by using these different substrates. Moreover the shape of a tip is important for reproducibility. The method for coating a silicon tip is as follows. Controlling the colloidal particle size was achieved by varying the concentration of silver nitrate solution (from 0.1 wt % to 0.5 wt %). Precise control of the temperature is quite important in this experiment. First, 120 μL of 0.3 wt % KOH solution was added to 3 mL of silver nitrate solution. A fine brown precipitate of Ag_2O was formed. To this mixture, 5 wt % ammonia solution was added in 10 μL drops until the precipitate completely dissolved to form $[Ag(NH_3)_2]^+$. Then, 6 wt % silver nitrate solution was added in 5 μL drops until the solution became pale yellow. The reducing agent was prepared by adding 0.5 mL of methanol to 1 mL of 35 wt % glucose solution, which was kept warm at 35 °C. The silver nitrate solution and reducing agent were then mixed at 35 °C, at which point the solution changed to black. A silicon tip was immersed in this solution and left for approximately 90 s, after that it was removed and sonicated for a few seconds with 1:1 mixture of distilled water:acetone and dried under nitrogen. A non-coated silicon AFM tip was purchased from MikroMasch (CSC12); this tip had a cantilever resonant frequency of $\approx$100 kHz and a force constant of $\approx$1 N/m. Characterization of the particle size distributions was performed by scanning electron microscopy (JEOL JSM-6330F).

The detailed experimental setup has been reported previously.[16] Laser excitation was provided by a 532-nm CW YAG laser ($\approx$1 mW at sample point). The sample was set on an inverted oil-immersion microscope objective lens ($\times$60, N.A. $=$ 1.4). The probe was put on the focus spot of the incident laser beam. The SERS signal was collected and detected by the same objective lens and detected by a triple spectrometer (slit width 200 μm) and liquid-nitrogen cooled CCD camera.

As the sample, carbon nanotubes were purchased from Carbon Nanotechnologies Inc. A 0.002 wt % solution of nanotubes in THF solution was sonicated for about 6 h. The solution was spin-coated on the cover slip and the solvent allowed to evaporate.

Figure 1 shows the average grain size of silver particles on

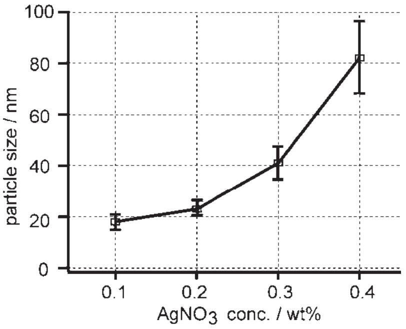

Figure 1. $AgNO_3$ concentration dependence of silver particle size.

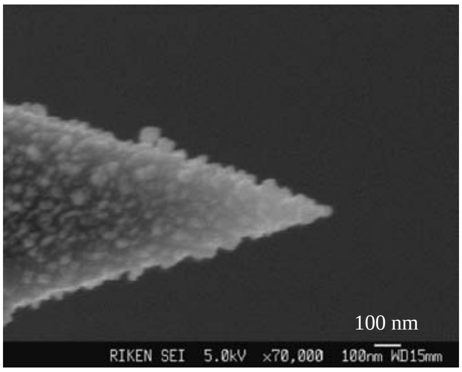

Figure 2. SEM image of silver-coated probes with ≈40-nm particles (5 kV, 12 μA, ×70,000).

silicon tips as a function of silver nitrate concentration. Among several possible reaction variables, such as temperature, reaction time, concentration of the reductant, etc., we found that the particle size was the most easily controlled by changing the concentration of the silver nitrate. From this figure, a suitable concentration for forming ≈40-nm particles is 0.3 wt %.

An SEM image of the coated probe is shown in Figure 2. This image shows complete surface coverage with good packing at the tip apex. The reproducibility of the particle size on the apex tip was 40 ± 6 nm. The particle shape produced by the mirror reaction is approximately spherical. In comparison, vacuum evaporated silver surfaces formed at an evaporation rate of 0.1 nm/s have typical grain diameters of 30 nm and heights of 5–10 nm.[17] For surface plasmon applications, such surfaces are usually annealed to increase the size and aspect ratio (height: width), but this procedure often bends the probe due to the differences in surface tension imposed on the two sides of the cantilever. In the present method, 40-nm particles are fixed at the probe apex without causing any damage to the cantilever. From the viewpoint of enhancement, an isolated spheroidal particle gives higher enhancement than an isolated spherical particle. However, in our scheme, a spherical particle is attached at a tip apex. The whole shape of the tip apex is no longer spherical which means that so-called lightning rod effect would be anticipated.[18] While the shape of the silver particles are also important subject for SERS enhancement, we have concentrated how to control the particle diameter in this letter. The shape control is under investigation.

To examine the performance of the probes, we measured tip-enhanced Raman spectra of carbon nanotubes in our near-field system. Figure 3a shows tip-enhanced Raman spectra of a carbon nanotube bundle obtained by the probes shown in Figure 2. We chose radial breathing modes (Raman shift ≈180–300 cm^{-1}) as a demonstration, because the symmetry of these modes is A_{1g} and they should be involved in the field enhancement. The thick solid line in Figure 3a shows the near-field spectra (obtained with silver tip), while the dotted line shows the far-field spectra (obtained without the tip) and the thin solid line represents the spectra produced by subtracting the far-field spectra from the near-field spectra. Laser intensity is quite stable during the measurement time of ≈60 s. We also sufficiently suppressed unwanted stray light by using evanescent focused illumination.[16] A clear enhancement due to the silver coated probe was observed. For example, the RBM at 276 cm^{-1} was enhanced more greatly than the other RBM, which means that the CNT having the RBM at 276 cm^{-1} existed just under the tip. Other tubes having different diameters were not beneath the tip, therefore the enhancement were weaker than the RBM of 276 cm^{-1}.

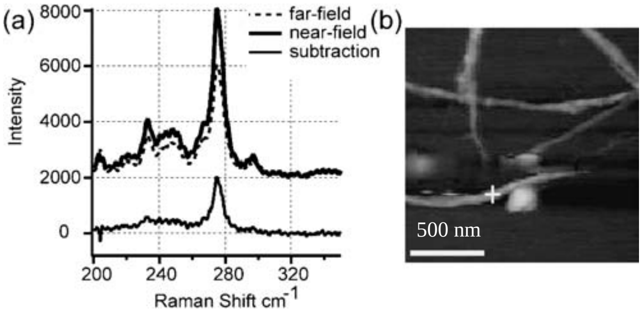

Figure 3. (a)Tip-enhanced Raman spectra of carbon nanotubes using silver-coated probes; 532-nm 1-mW excitation, 60-s accumulation time, ×60, 1.4-NA objective. (b)AFM images of carbon nanotubes. Contact mode, 0.4-Hz line scan, resonance frequency 100 kHz, 1.5 μm × 1.5 μm, 256 × 256 pixels. The cross shows the point where the tip was placed during the Raman spectra measurements presented in (a).

Figure 3b shows an AFM image measured by the same probe. The cross indicates the position of the probe during the tip-enhanced measurement. This figure demonstrates that the silver coated tips can be used for AFM scanning and therefore show potential for being used as near-field Raman imaging probes.

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