Preparations of Triangular Gold Nanoplates by Chemical and Photoreduction Methods

Makoto Takezaki, Ryosuke Kida, Yuya Kato, and Toshihiro Tominaga*
Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700-0005

(Received August 3, 2009; CL-090720; E-mail: tominaga@dac.ous.ac.jp)

Triangular gold nanoplates were prepared both by chemical and photoreduction methods. Uniformly sized nanoplates were obtained and their extinction spectra agree with those calculated by discrete dipole approximation with aspect ratios obtained by a transmission electron microscope.

Metal nanoparticles show unique properties that are different from those of bulk metals.[1,2] Silver and gold triangular nanoprisms and nanoplates display interesting localized surface plasmon resonances.[3–11] They are particularly of interest in that the electromagnetic field is enhanced around the vertices of the particles. Furthermore, when two or more triangular particles meet, the enhancement is magnified which is expected to significantly affect spectral properties such as surface-enhanced Raman scattering.[12–14] Recently much effort has been directed toward preparing triangular gold nanoprisms and nanoplates.[15–20] We would like to report here simple chemical and photoreduction methods to prepare triangular gold nanoparticles.

In the chemical reduction method, we used tartaric acid as the reducing agent and hexadecyltrimethylammonium chloride (CTACl) as the protective agent. A solution containing 0.5 mM ($1\,\mathrm{M} = 1\,\mathrm{mol\,dm^{-3}}$) $HAuCl_4$, 2.2 mM CTACl, and 45 mM tartaric acid was placed in an oil bath kept at 40 °C. After standing for 10 min, the bath temperature was increased to 67 °C, where the reaction took place for 10 min, after which the solution was taken out of the bath. Transmission electron microscope (TEM) observations were made using a Hitachi H-8100 TEM with 200-kV acceleration voltage. Figure 1 shows TEM images of the nanoparticles obtained. Figure 1a shows a typical example of two-dimensionally arranged triangular nanoplates with side lengths of 54 ± 9 nm, and Figure 1b shows that their thickness is 15 nm. In Figure 1a, some particles appear to be diamonds, but a magnified image shows that they are triangles (Figure S1).[21] TEM and selected area electron diffraction (SAED) images obtained using a JEOL JEM-4000EX TEM with 400-kV acceleration voltage are shown in Figure S2,[21] where the SAED pattern shows that the particle is a single-crystalline gold with (111) main face. In Figure 1b, some particles may appear to be rods, but they are seen to be triangular plates when TEM images are taken with tilted angle (Figure S3).[21]

In the photoreduction method, we used a 500-W high-pressure mercury lamp (Ushio UI-502Q).[22] After nitrogen bubbling, aqueous solutions containing $HAuCl_4$, CTACl, HCl, and KCl in a quartz cuvette (1-cm path length) were irradiated by a collimated beam from the lamp for 3 h at 35 °C. After the reaction, the solution was allowed to stand for 30 min, and the purple supernatant solution, which contained smaller spherical particles and rods, was discarded. The sediments were dispersed by adding water, and larger particles were separated by centrifugation. Figure 2 shows a TEM image of particles with side length of 100 nm (Figure 2a) and thickness of 8 nm (Figure 2b) obtained by irradiating the solution containing 2.1 mM $HAuCl_4$, 3.5 mM CTACl, 150 mM HCl, and 66 mM KCl. When the HCl concentration was 50–150 mM and the KCl concentration was 30–70 mM, similar results were obtained.

Figure 3 shows the extinction spectra for our triangular plates. The 54-nm side length gold nanoplates show a peak at 550 nm and a tail extending up to about 800 nm, whereas those of 100-nm side length display two broad extinction peaks at 593 and 850 nm. In order to examine these peak wavelength differences, we calculated extinction spectra for two perfect gold triangular nanoplates with side lengths of 54 and 100 nm with different ratios of the side length to the thickness, i.e., aspect ratio (R), by discrete dipole approximation (DDA)[23] using the gold dielectric function.[24] The calculated extinction spectra are shown in Figure 4. The R value dependence of the major peak wavelengths, λ, (longer than 600 nm) for the two different plates is shown in Figure S4.[21] The $\lambda_{\max}$ values increase linearly with increasing R value and are expressed as

$$\lambda_{54\,\mathrm{nm}} = 544.4 + 17.7R \qquad (1)$$

$$\lambda_{100\,\mathrm{nm}} = 601.7 + 17.7R \qquad (2)$$

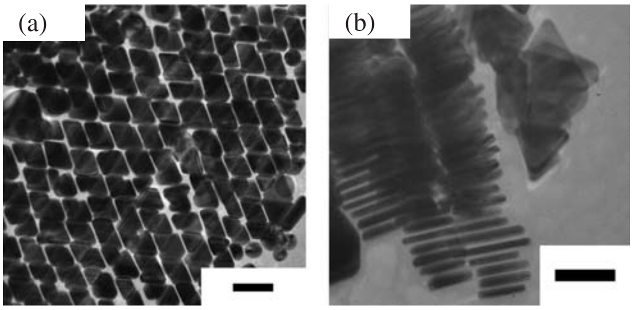

Figure 1. TEM images of the gold nanoparticles obtained by tartaric acid reduction of $HAuCl_4$ in the presence of CTACl. Scale bars: 100 nm.

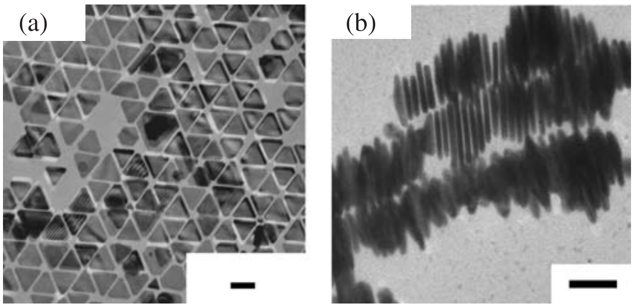

Figure 2. TEM images of the gold nanoparticles obtained by photoreduction of $HAuCl_4$ in the presence of CTACl, HCl, and KCl. Scale bars: 100 nm.

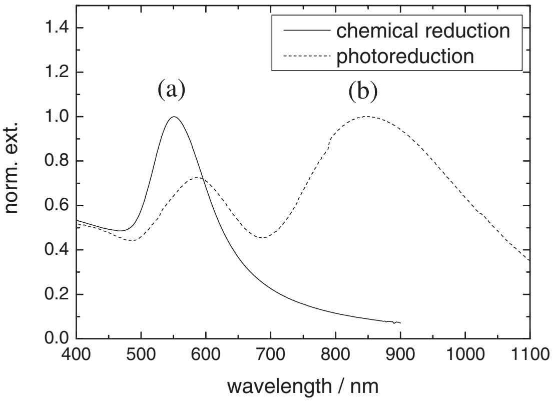

Figure 3. Extinction spectra of the gold nanoparticles obtained by tartaric acid reduction (a) and photoreduction (b).

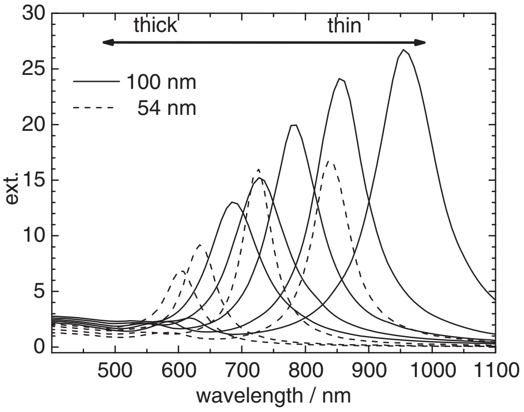

Figure 4. Calculated extinction spectra for the 54- and 100-nm gold nanoplates of various thicknesses, 5, 7, 10, 15, and 20 nm for the 100-nm plate and 3, 5.4, 10.8, and 15.2 nm for the 54-nm plate. Solid lines: 100-nm plate. Dashed lines: 54-nm plate.

for the 54- and 100-nm plates, respectively. These peaks are due to the in-plane dipolar plasmon resonances. In Figure 4, there are small peaks for the 100-nm plates at 583 and 617 nm for 7- and 5-nm thicknesses, respectively. These peaks are due to the in-plane quadrupolar resonance.

From the TEM observation in Figure 1b, the 54-nm plate thickness is about 15 nm. For this plate, the R value is 3.6, and the peak wavelength is calculated to be 608 nm using eq 1. This calculated wavelength is 58 nm longer than the peak wavelength for our 54-nm plate (550 nm). In the case of triangular silver nanoplates, the calculated peak wavelengths are reported to be blue-shifted with increasing snip length.[4] The 58-nm wavelength difference of our 54-nm plates could be explained by some degree of snipping.

From the TEM observations the thickness of the 100-nm plate is about 8 nm which corresponds to an R value of 12.5. Substituting this value into eq 2, the peak wavelength is obtained to be 823 nm, which is close to the observed value (850 nm in Figure 3b). Alternatively if we substitute the observed peak wavelength (850 nm) into eq 2, the R value is obtained to be 14. From this value, the thickness is calculated to be 7.1 nm, which is close to the thickness of 8 nm obtained from the TEM observation. Thus, the calculated extinction spectrum may assist in determining the actual plate thickness when the thickness determination is difficult. The other extinction peak at 593 nm (Figure 3b) is higher than that from DDA (Figure 4), which would be due to the presence of smaller particles.

In summary, we prepared two kinds of size-controlled triangular gold nanoplates, whose extinction spectra agree fairly well with those calculated by DDA.

The authors thank Prof. M. Fukuhara (Okayama University of Science) and Dr. Y. Kusano (Kurashiki University of Science and the Arts) for helpful discussions. This work was supported by MEXT.HAITEKU (2006–2008).

References and Notes

1 *Nanoparticles: From Theory to Application*, ed. by G. Schmid, WILEY-VCH, Weinheim, **2004**.
2 *Metal Nanoparticles: Synthesis, Characterization, and Applications*, ed. by D. L. Feldheim, C. A. Foss, Jr., Marcel Dekker, New York, **2002**.
3 R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **2001**, *294*, 1901.
4 K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B* **2003**, *107*, 668.
5 J. E. Millstone, S. Park, K. L. Shuford, L. D. Qin, G. C. Schatz, C. A. Mirkin, *J. Am. Chem. Soc.* **2005**, *127*, 5312.
6 A. Brioude, M. P. Plieni, *J. Phys. Chem. B* **2005**, *109*, 23371.
7 I. Pastoriza-Santos, L. M. Liz-Marzán, *J. Mater. Chem.* **2008**, *18*, 1724.
8 J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, S. Schultz, *J. Chem. Phys.* **2002**, *116*, 6755.
9 K. L. Shuford, M. A. Ratner, G. C. Schatz, *J. Chem. Phys.* **2005**, *123*, 114713.
10 L. J. Sherry, R. C. Jin, C. A. Mirkin, G. C. Schatz, R. P. Van Duyne, *Nano Lett.* **2006**, *6*, 2060.
11 T. Uwada, T. Asahi, H. Masuhara, D. Ibano, M. Fujishiro, T. Tominaga, *Chem. Lett.* **2007**, *36*, 318.
12 E. Hao, G. C. Schatz, *J. Chem. Phys.* **2004**, *120*, 357.
13 M. Suzuki, Y. Niidome, Y. Kuwahara, N. Terasaki, K. Inoue, S. Yamada, *J. Phys. Chem. B* **2004**, *108*, 11660.
14 K. Imura, H. Okamoto, M. K. Hossain, M. Kitajima, *Chem. Lett.* **2006**, *35*, 78.
15 H.-C. Chu, C.-H. Kuo, M. H. Huang, *Inorg. Chem.* **2006**, *45*, 808.
16 W.-L. Huang, C.-H. Chen, M. H. Huang, *J. Phys. Chem. C* **2007**, *111*, 2533.
17 T. H. Ha, H.-J. Koo, B. H. Chung, *J. Phys. Chem. C* **2007**, *111*, 1123.
18 J. E. Millstone, W. Wei, M. R. Jones, H. J. Yoo, C. A. Mirkin, *Nano Lett.* **2008**, *8*, 2526.
19 J.-H. Lee, K. Kamada, N. Enomoto, J. Hojo, *Cryst. Growth Des.* **2008**, *8*, 2638.
20 J. E. Millstone, S. J. Hurst, G. S. Métraux, J. I. Cutler, C. A. Mirkin, *Small* **2009**, *5*, 646.
21 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
22 D. Ibano, Y. Yokota, T. Tominaga, *Chem. Lett.* **2003**, *32*, 574.
23 a) B. T. Draine, P. J. Flatau, *J. Opt. Soc. Am. A* **1994**, *11*, 1491. b) B. T. Draine, P. J. Flatau, *User Guide to the Discrete Dipole Approximation Code DDSCAT 7.0*, **2008**, http://arXiv.org/abs/0809.0337v5.
24 P. B. Johnson, R. W. Christy, *Phys. Rev. B* **1972**, *6*, 4370.