Transactions of the Materials Research Society of Japan 27 [1] 159-161 (2002)

Shape Controls of Electrochemically Prepared Gold Nanorods

Tsuguo Onishi, Hiroshi Yao,* Seiichi Sato and Keisaku Kimura
Department of Material Science, Faculty of Science, Himeji Institute of Technology,
3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan
Fax: 81-791-58-0161, e-mail: yao@sci.himeji-tech.ac.jp

Gold nanorods were prepared in aqueous micelles with ionic surfactants composed of the supporting electrolyte surfactant (hexadecyltrimethylammonium bromide) and a shape-inducing cosurfactant by an electrochemical method. During the syntheses, a gold plate as the anode is converted sacrificially to form nanorods. We examined the effects of cosurfactants and/or silver ion release from the immersed silver plate on aspect ratios of the obtained nanorods. Cosurfactants play a crucial role for determining the shapes of the rods. By controlling these factors, the gold nanorods are grown to be submicrometers in length with a very high aspect ratio (mean aspect ratio: 18).

Key words: nanorod, aspect ratio, gold, electrochemical method, micelle

1. INTRODUCTION

Nanostructured materials are attracting much attention due to their potential use in technological applications [1]. Since the electronic, magnetic, optical and/or catalytic properties of these materials depend highly on their size and shape, one of the desired goals is the morphological controls of nanostructured materials [2]. A great deal of methods have been developed to synthesize spherical nanoparticles of different sizes while the shape control of these particles still remains a preparative challenge.

Recently, gold nanorods have been synthesized in aqueous media by using a rigid template of mesoporous alumina [3] and by an electrochemical method in the presence of cationic surfactant systems [4-6]. The electrochemical method has characteristic features in controlling the cylindrical growth of gold by adding a shape-inducing micellar reagent (cosurfactant) into the electrolysis system in which appropriate surfactants exist as both the supporting electrolyte and the stabilizer. This method is expected to be practical for easy isolation and large-scale synthesis of nanorods.

In the electrochemical systems, the aspect ratio (the ratio of length to width) of the prepared nanorods can be substantially controlled by changing the molar ratio of the two surfactants. It is also reported that a slow silver ion release into the electrolytic solution would affect the long-axis length of the nanorods [4]. However, gold nanorods with high aspect ratio larger than ~7 have been rarely prepared mainly because the surfactants used were limited [6]. In the present work, we report an electrochemical preparation of gold nanorods with high aspect ratios (mean aspect ratio: 18) in aqueous solutions by controlling the cosurfactant systems and the constituents of the electrochemical cell. The rods are finally grown to be submicrometers in length; one of the highest aspect ratio rods prepared in the absence of a rigid mesoporous template at the present stage [7].

2. EXPERIMENTAL

2.1 Synthesis of Gold Nanorods

Gold nanorods were prepared by an electrochemical method similar to those described in the literatures [4-6], however, some modifications were employed.

Briefly, the syntheses were conducted within a simple two-electrode-type electrochemical cell consisting of a gold electrode (30 x 10 x 0.5 mm) as the sacrificial anode and a platinum electrode (30 x 10 x 0.5 mm) as the cathode. Both electrodes were fixed in place by using a dielectric spacer with the distance of ~2.5 mm. Typically, the electrolytic solution consisted of a 8.0×10^{-2} M hexadecyltrimethylammonium bromide (abbreviated as HTAB, Wako Pure Chemicals) as the supporting electrolyte surfactant, and a 5.4×10^{-3} M hydrophobic cosurfactant. The incorporation of a hydrophobic cosurfactant into the HTAB micellar framework would induce a cylindrical micellar shape to support the cylindrical growth of nanometer-sized gold [5]. The electrolysis was carried out for 20 min with a constant applied current of 10 mA at ~40 °C under continuous ultrasonication. During the synthesis, the bulk gold metal was converted from the anode to form mixtures of nanoparticles and nanorods in solution. Thus, the nanorods were separated by centrifugation with a Kubota 1720 centrifuge.

Based on the procedures described above, three samples were prepared as follows. For the preparation of sample **a**, tetradodecylammonium bromide ($TC_{12}AB$, Wako Pure Chemicals) was used as the hydrophobic cosurfactant. Moreover, a silver plate (30 x 10 x 0.5 mm) was immersed in the solution behind the platinum electrode during the electrolysis. For sample **b**, tetrabutylammonium bromide (TC_4AB, Wako Pure Chemicals) was used as the cosurfactant in the presence of the silver plate in the electrolyte solution. In the case of sample **c**, TC_4AB was used as the cosurfactant in the absence of the silver plate. Other experimental conditions were the same among the samples **a-c**.

2.2 Apparatus

Transmission electron microscopy (TEM) was conducted by a Hitachi-8100 electron microscope operated at 200 kV. TEM grids for the observations were prepared by placing a diluted particle solution on a micro-grid and dried at room temperature. Selected area electron diffraction pattern was obtained at a camera length of 1 m. Absorption spectra were measured with a Hitachi U-3210 spectrophotometer by using cuvettes with 1-cm optical path length.

3. RESULTS AND DISCUSSION

3.1 Effect of Cosurfactants on the Shapes of Gold Nanorods

Figures 1a and 1b show typical TEM images of the samples **a** and **b**, respectively. Distinctive nanorods were observed with a narrow distribution of short-axis lengths and a slightly broad distribution of long-axis lengths. From the images, the mean short-axis length and the aspect ratio of gold nanorods for sample **a** were about 12.4 nm and 5.4, respectively, while those for sample **b** were 7.5 nm and 4.8, respectively. The mean aspect ratios were almost unchanged between the samples **a** and **b**. Consequently, the cosurfactant TC_4AB plays an important role for reducing both the short-axis and the long-axis lengths of the rods under a constant aspect ratio. The results also imply that a selection of cosurfactant molecules can lead to thinner nanorod formation.

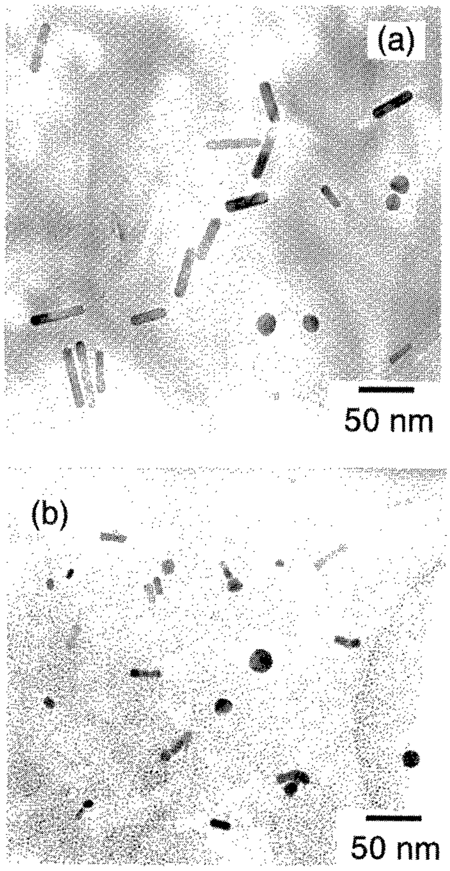

Fig.1 (a) and (b) show the TEM images of gold nanorods for samples **a** and **b**, respectively.

An electron diffraction pattern of the rod ensembles clearly shows several bright rings composed of strong spots (Fig. 2), and the lattice spacings based on the pattern were calculated to be 2.37, 2.05, 1.40, 1.27, and 0.948 Å that are assigned to the (111), (200), (220), (311), and (331) reflections of crystalline gold, respectively. The results indicate that the prepared nanorods does not possess silver inclusions in spite of the occurrence of a silver ion release into the solution [4].

It has been demonstrated that the surface plasmon resonances of the gold nanoparticles sensitively depend on not only the particle sizes but also the particle morphologies [3,8]. Therefore, we measured absorption spectra of samples **a** and **b** as shown in Fig. 3. The absorption spectra are characterized by a longitudinal surface plasmon band (SP_L) observed at longer wavelength and a transverse plasmon band (SP_T) at shorter wavelength. It is known that the position of the SP_L band is subject to a shift according to the aspect ratios of the rod [8]. Judging from the fact that the peak position of the SP_L band of the sample **b** (~750 nm) was similar to that of sample **a** (~743 nm), the aspect ratio of gold nanorods for sample **b** must be almost unchanged compared to that of sample **a**. The results are consistent

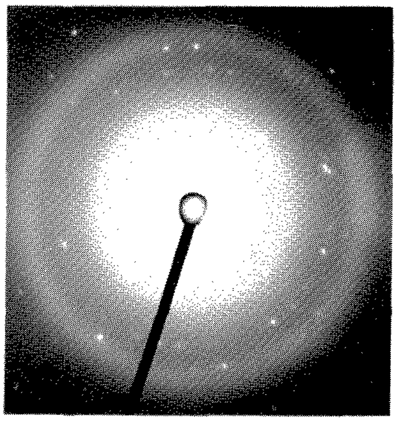

Fig. 2 Electron diffraction pattern of sample **a**.

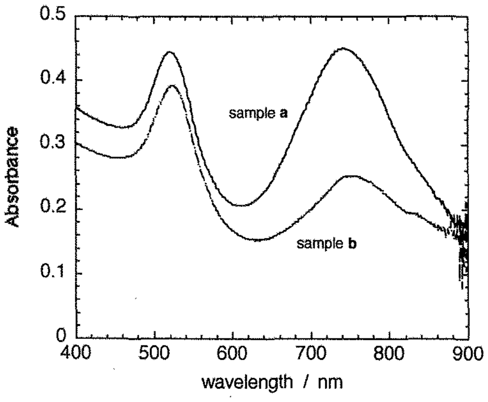

Fig. 3 Absorption spectra of gold nanorods for samples **a** and **b**. The absorption peak at 523 nm or ~750 nm is ascribed to the transverse or the longitudinal surface plasmon resonance, respectively.

with those obtained by the TEM measurements. It should be noted that an additional contribution to the absorbance of the SP_T band would come from the gold nanospheres existing in the solution. According to Fig. 3, the lower ratio of the absorbance of the SP_L to SP_T band was obtained for sample **b** than that for sample **a**. The result is due to an inclusion of larger amounts of gold nanospheres in sample **b** as revealed by the TEM.

3.2 High Aspect Ratio Gold Nanorods

So far, a silver plate was immersed behind the platinum electrode inside the solution for the aid of supposed cylindrical growth of gold nanorods at an electrochemical preparation [4-6]. However, silver ions released from the plate render the system considerably complex, and might cause a contamination for the obtained nanorods. Therefore, nanorod preparations in the absence of other metal components such as a silver plate is a vital challenge. We examined here the effects of the silver plate on the formation of gold nanorods.

Fig. 4 shows a typical TEM image of sample **c**, which was electrochemically prepared with TC_4AB in the absence of a silver plate. Gold nanorods with very high aspect ratios can be seen in the image along with gold nanospheres. At the present stage, separation of nanorods from the sphere/rod mixtures by centrifugation was insufficient because the nanospheres were likely to form aggregates in this sample. However, the aspect ratio of the gold nanorods ranged between ~8 and 30, and the mean aspect ratio was obtained to be 18; one of the highest values in solution syntheses without using a rigid mesoporous template [7]. Furthermore, the rods were grown to be submicrometers in length. On the other hand, the mean short-axis length of the rods was 22.4 nm, which is larger than that of sample **b** prepared in the presence of the silver plate. Because the soft micellar template is considered to contribute the rod formation by the shape-inducing cosurfactants, the results indicate that a release of silver ions from the silver plate greatly affects the shape-inducing properties of the cosurfactant.

Note that gold nanorods could not be prepared by using cosurfactant $TC_{12}AB$ in the absence of a silver plate, although TC_4AB led to formation of very long rods. The results suggest that there exists large differences in the structures of template micelles and/or in the growth mechanisms between them.

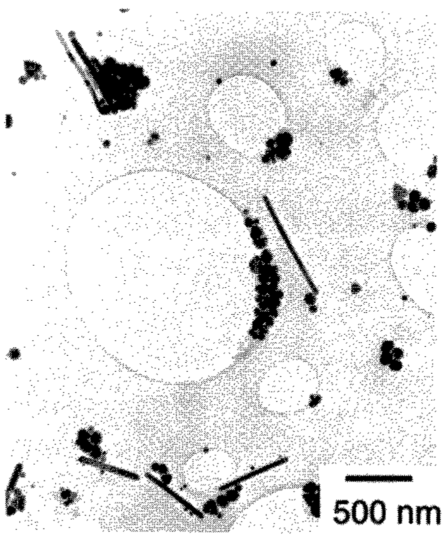

Fig. 4 TEM image of gold nanorods for sample **c**.

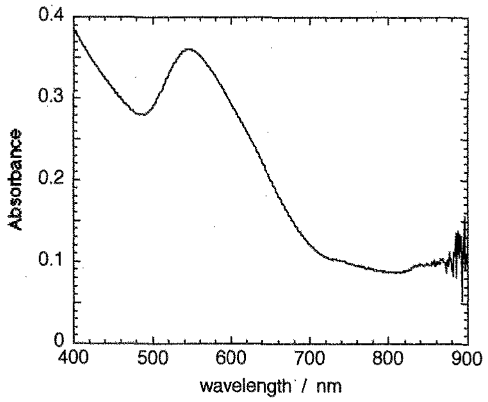

Fig. 5 Absorption spectrum of gold nanorods for sample **c**.

Fig. 5 shows absorption spectrum of sample **c**. We did not observe an SP_L band for this sample within the confines of our scan. This result is reasonable because the SP_L band should appear at a longer wavelength region. The broad peak at 545 nm is probably due to a conventional surface plasmon band of sphere nanoparticles included in the solution because an SP_T band of nanorods is expected to be slightly blue-shifted with increasing aspect ratio [9].

In summary, we demonstrated that the aspect ratios of gold nanorods can be controlled by adjusting the growth conditions; especially, the choice of cosurfactants plays a crucial role for the synthesis of the very long gold nanorods with high aspect ratios.

ACKNOWLEDGMENT. H.Y. acknowledges the partial financial support from Tanaka Kikinzoku Kogyo.

REFERENCES

[1] A. P. Alivisatos, *Science*, **271**, 933-937 (1996).

[2] A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **101**, 1562-1572 (1997).

[3] B. M. I. van der Zande, M. R. Böhmer, L. G. J. Fokkink and C. Schönenberger, *J. Phys. Chem. B*, **101**, 852-854 (1997).

[4] S.-S. Chang, C.-W. Shih, C.-D. Chen, W.-C. Lai and C. R. C. Wang, *Langmuir*, **15**, 701-709 (1999).

[5] Y.-Y. Yu, S.-S. Chang, C.-L. Lee and C. R. C. Wang, *J. Phys. Chem. B*, **101**, 6661-6664 (1997).

[6] S. Link and M. A. El-Sayed, *J. Phys. Chem. B*, **103**, 8410-8426 (1999).

[7] N. R. Jana, L. Gearheart and C. J. Murphy, *J. Phys. Chem. B*, **105**, 4065-4067 (2001).

[8] S. Link, M. B. Mohamed and M. A. El-Sayed, *J. Phys. Chem. B*, **103**, 3073-3077 (1999).

[9] B. M. I. van der Zande, M. R. Böhmer, L. G. J. Fokkink and C. Schönenberger, *Langmuir*, **16**, 451-458 (2000).

(Received December 21, 2001; Accepted January 17, 2002)