RSC Advances

growth
solution

citrate-stabilized
seeds

Surfactant Gel

One-pot synthesis

Twin AuNR

1755.2 ± 406.0 nm

97x46mm (300 x 300 DPI)

Journal Name

ARTICLE

One-pot synthesis of long twin gold nanorods in a gelled surfactant solution

Y. Takenaka,[a,b]

A new one-pot synthesis method was developed for producing long twin gold nanorods with lengths of ca. 1755 nm, which have a potential to be arranged on a substrate using anisotropic surface modification. This method was achieved by using citrate-stabilized seeds in a gelled surfactant solution, i.e., in the mixture of hexadecyltrimethylammonium bromide and octadecyltrimethylammonium bromide at low temperature (20 °C). The yield (ca. 60 %) of this method is relatively high. The mechanism of the present growth conditions were compared with those reported in previous studies. As expected, NO_3 had an influence on the length of the gold nanorods and the longest ones were obtained at an optimal concentration of NO_3, even for growth in the gelled surfactant solution. In contrast, the number of seeds in the growth solution had no effect on the lengths of the nanorod grown in the gelled surfactant.

Introduction

Recently, many types of nanomaterials have been extensively studied for the development of various applications. Gold nanorods are possibly one of the most interesting nanomaterials. The length of these nanorods ranges from several tens of nanometers to values exceeding 1 μm. The long nanorods, especially those longer than 1 μm, are well-suited for use as electrodes,[1] nanogap electrodes,[2,3] nanorod arrays,[4-8] and new photonic devices.[9]

It is well established that there are two kinds of crystal structures in gold nanorods, namely, single crystal and twin. Twin gold nanorods have different crystal planes at the sides and edges of the nanorods; (100) or (110) and (111) planes are located at the sides and edges, respectively. Moreover, twin gold nanorods, especially those longer than 1 μm, are easily manipulated and modified the surfaces in anisotropic way, whereby the side and edge are modified with different molecules. For further application, these twin gold nanorods will be arranged or moving on a specially-patterned surface by means of the anisotropic interaction between the two surfaces. So, long twin gold nanorods are really to be acquired.

Twin gold nanorods are typically synthesized using a stepwise additive method.[10,11] In this method, citrate-stabilized seeds are added to the growth solution that contains the surfactant, Au ions, and the reducing agents. Some of the mixture is then added to another growth solution, which is composed of the same constituents and the process is repeated.

As reported by Wu et al.,[12] long twin gold nanorods can be synthesized in a growth solution that contains NO_3. This method yields a relatively high, ca. 60-70 %, fraction of nanorods, albeit with limited lengths of 400-500 nm. Chen et al. obtained 1.4 μm twin gold nanorods by increasing the number of steps in the growth process;[13] in that case the gold nanorods were synthesized in 4 growth steps. Furthermore, Critchley et al. obtained 2.3 μm long twin nanowires (including an

additional overgrowth) after 3 steps of growth.[14] Several steps and procedures must be performed in order to synthesize long twin gold nanorods by means of the aforementioned methods. A simple one-step synthesis method for these nanorods is, therefore, required.

In this work, a new one-pot synthesis method was developed to produce twin gold nanorods which have lengths of over 1 μm. Yield of 90 % were reported in the case of long gold nanorods (with lengths exceeding 1 μm) that were grown in a gelled surfactant solution with the seed stabilized with surfactant.[15] This gelation method was applied to the citrate-stabilized seeds used in the current investigation. As a result, yield of ca. 60 % of high-aspect-ratio twin gold nanorods, with lengths of over 1 μm, could be obtained from the gelled growth solution that contains NO_3. Gole et al. investigated the effects of charge or size of various kinds of seeds on the shape or yield of ~500 nm long nanorods.[16] However, the effects of the citrate-stabilized seeds on the resulting length have not been investigated for nanorods longer than 1 μm. In addition to Gole et al., Murphy et al. also investigated the effect of the seeds used. They reported that the optical spectra and dimensions of the final gold nanorods do not depend on the crystalline nature of the gold core when the nanorods grow in aqueous surfactant solution.[17] The growth of the nanorods with citrate-stabilized seeds in a gelled surfactant solution was, however, not discussed and is, therefore, investigated in the present work. Furthermore, this study uses different NO_3 conditions and number of seeds from those of previous investigations. As such, these corresponding effects on the nanorod length are discussed for synthesis performed with and without gelation of the growth solution.

Experimental

Citrate-stabilized seeds were synthesized as described alsewhere.[12] An aqueous solution containing 19.8 ml of 0.25

mM hydrogen tetrachloroaurate(III) tetrahydrate (HAuCl$_4$: Nacalai Tesque) was mixed with 200 µl of 25 mM trisodium citrate dihydrate (Citrate: Kanto Chemical Co., INC.) solution in a clean glass bottle. The concentrations of HAuCl$_4$ and citrate are both 0.25 mM. Then 10 ml of 10 mM sodium borohydride (NaBH$_4$: Nacalai Tesque) solution was prepared by adding NaBH$_4$ to 10 ml of ice-cold 25 mM sodium citrate solution. 0.6 ml of this NaBH$_4$ solution was added to the mixed solution of HAuCl$_4$ and citrate and vigorously stirred. Stirring was continued for 2 min after the addition of the NaBH$_4$ solution in order for the evolved gas to be released. The resulting orange-red suspension of gold seeds was stored at room temperature (ca. 20 °C) for 2 h.

The growth solution was prepared as follows. The mixed surfactant solution with 100 mM of hexadecyltrimethylammonium bromide (HTAB: Tokyo Chemical Industry Co., LTD.) and 75 mM of octadecyltrimethylammonium bromide (OTAB: Wako Pure Chemical Industries, Ltd.) was prepared at 60 °C (in this case, the total concentration of surfactants was 175 mM).[18] A portion (9.5 ml) of this mixure, 237.5 µl of 10 mM HAuCl$_4$ aqueous solution, 64 µl of 100 mM L(+)-Ascorbic Acid (AA: Nacalai Tesque) solution, and 75 µl of 100 mM nitric acid (HNO$_3$; Kanto Chemical Co., INC.) were then mixed in a clean glass bottle. After the temperature of the mixed solution decreased to around room temperature, 17 µl of the seed suspension was carefully added and the solution was mixed gently for 10 s. This solution was then kept at 20 or 40 °C overnight, using a thermostat bath (PCl-101, As One). The final concentrations of HTAB, OTAB, HAuCl4, AA, and NO$_3$ were 95.9, 71.9, 0.25, 0.66, and 0.78 mM, respectively.

The nanorods were stabilized by adding 500 µl of 1% dodecanethiol (C$_{12}$H$_{25}$SH; Wako Pure Chemical Industries, Japan) in ethanol (99.5 %, Wako Pure Chemical Industries, Japan) solution to the resulting aqueous gold-nanorod suspensions.[24] The stabilized nanorods could then be examined by scanning electron microscopy (SEM: S-4800, Hitachi). In the case of the gelled suspensions, 1% dodecanethiol in ethanol solution was added after dissolving the suspension at 60 °C. Then, 1400 µl of the resulting suspension was centrifuged at 5000 rpm for 5 min, and the transparent supernatant portion was removed. The residual portion was re-dispersed in 700 µl of pure water (Direct-Q 5UV, Millipore SAS) and re-centrifuged at 5000 rpm for 5 min. After the supernatant portion was removed again, the residual dense suspension was used to prepare the SEM samples.

SEM samples were prepared by sonicating the Si substrate for 5 min each in pure water and in ethanol (95 %, Wako Pure Chemical Industries, Japan), and then blowing with N$_2$. Then, 10 µl of the suspension was placed on the Si substrate for 2 min. After removing the excess suspension, the substrate was dried in a desiccator and subsequently used for SEM observations.

Results and Discussion

Figure 1 shows the SEM images of the gold nanorods grown at 20 °C and 40 °C. The gold nanorods grown at 20 °C (1755.2 ± 406.0 nm) was much longer than those grown at 40 °C (435.3 ± 70.5 nm). The same tendency was observed in a previous study where the seeds were stabilized by surfactants.[15] This phenomenon was thought to result from the gelation of the growth solution instead of the stabilization of the molecules of the seeds.

The Krafft temperature (so-called gelation temperature) of the mixed surfactant solution used was assumed to be in the range of 26 and 38 °C, since the corresponding temperatures of HTAB and OTAB are 26 and 38 °C, respectively.[22,25] This implies that the surfactant molecules in the growth solution form a coagel structure (a periodic structure of solid bilayer membranes separated by water layers; i.e., the so-called lamellar structure), and micelles[26] at 20 and 40 °C, respectively.

The effects of gelation on the elongation of nanorods were explained for long nanorods that organized from surfactant-stabilized seeds. The higher stability of the complexes between Au ions and the lamellar structure than those between Au ions and micelles was thought to contribute to the elongation of the nanorods.[19] Since these complexes are formed by the electrostatic interaction between anionic Au ions and cationic surfactants, their formation is not directly related to the stabilized molecules of the seeds. Therefore, the seeds do not have effect on the stability of the complexes. As such, long nanorods can grow in the gelled surfactant solution with the citrate-stabilized as well as with the surfactant-stabilized seeds.

Figure 1c shows the diffraction pattern of an edge part of a gold nanorod grown at 20 °C. There are two series of spots which originate from different crystalline structures in this diffraction pattern. Based on the correspondence between this diffraction pattern and those reported by Johnson et al., the gold nanorods in Fig. 1a were determined as a twin crystal structure.[27,28] This result showed that long twin nanorods, with lengths exceeding 1 µm, can be grown in a gelled surfactant solution with citrate-stabilized seeds. However, the corresponding yield, 60.8 %, was lower than that of the gold nanorods grown with surfactant-stabilized seeds (87.0 %).[15] This low yield may have resulted from the trisodium citrate-assisted growth of nanoplates.[28,29]
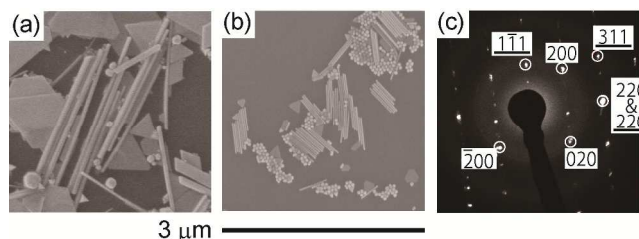

Figure 1. Gold nanorods grown at different temperatures. SEM images of gold nanorods grown at (a) 20 °C (1755.2 ± 406.0 nm) and (b) 40 °C (435.3 ± 70.5 nm). (c) Diffraction pattern of one of the gold nanorods in (a). The indices with and without underlines mean two different series of spots.

The present growth condition is discussed hereafter. There are two important processes when the seeds grow up to nanorods. One is the process where the anisotropic growth occurs. The anisotropic growth occurs because of the difference in binding strength of surfactant molecules on each crystal facets of seeds. Surfactants bind stronger to (100) or (110) planes than to (111) plane, and therefore Au ions can bind easier to (111) plane than other planes. Then (111) plane grows preferentially and anisotropic growth occurs[28,31].

The other important process is the process where the diameter and length of nanorods are determined by the growth condition. In this paper, the latter will be focused on. Factors which were reported to affect the elongation of the nanorods were surveyed, and the differences between the previous and current growth conditions were itemized. In addition, the

effects of each of the differences on the elongation of the nanorods were analyzed.

Many factors have been reported to affect the elongation of anisotropic cores of gold nanorods. These include the concentration of surfactants in the growth solution,[19] the ratio[21] of [Br$^-$]/[Au^{3+}], the stabilization[32] of Au ions as [AuBr$^-$], an electrostatic field at the edge of the nanorods,[20] small amounts of halide ions in the growth solution,[11,33,34] growth temperature,[35] self-assembly of the surfactants as a template of gold nanorods,[36-38] additives,[12] the number of crystal nuclei,[19,39] and the pH of the growth solution.[40]

The concentration of surfactants in the growth solution was the same with the report of our previous study; a mixed surfactant solution containing 100 mM HTAB and 75 mM OTAB was used. The [Br$^-$]/[Au^{3+}] ratio was also the same because the concentrations of Au and Br ions, which were supplied by the surfactants, were the same. Similarly, the stabilization of Au ions as [AuBr$^-$] will have the same effects. The electrostatic field at the edge of the nanorods should be affected by the shape of nanorods and not by the types of seeds. Halide ions were not added in either set of experiments. Moreover the same growth temperature was used in both cases. The self-assembly of the surfactants as a template were thought to produce the same effects since the assembly was determined by the surfactant concentration and the temperature of the growth solution, and these two were the same. However, NO$_3$ was not added in the previous study[15] and should, therefore, represent a distinct difference between the two investigations. The number density in the seed dispersion appeared to differ between the previous and current studies, since the synthetic procedure of the seeds was different. Furthermore, the pH of the growth solution is also expected to be different owing to the addition of a strong acid, i.e., NO$_3$, and citrate-stabilized seeds in the present method. Thus, we should examine the effects of the following three factors on the elongation of nanorods in the present method: the concentration of NO$_3$, the number of seeds, and the pH in the growth solution.

The effects of the concentration of NO$_3$ on the length of the nanorods will be discussed first. The length of the nanorods was examined as a function of the amount of NO$_3$. Wu et al.[12] synthesized gold nanorods with citrate-stabilized seeds in a non-gelled solution. They indicated that the presence of nitride ions, rather than the slight pH change caused by the nitric acid, has a great effect on the formation of long nanorods. Therefore, based on those findings, the concentration of NO$_3$ was varied in the present experiments and the effects on the resulting length of nanorods were noted. Growth solutions were prepared with 0, 25, 50, 75, and 100 μl of 100 mM of HNO$_3$. The corresponding concentrations of NO$_3$ in these growth solutions are 0, 0.26, 0.52, 0.78, and 1.0 mM, respectively. Figure 2 shows the SEM images of gold nanorods grown with different concentrations of NO$_3$. The length and the yield of the nanorods in each case are summarized in Table S1. Figure 2 and Table S1 show that the length of the nanorods is affected by the concentration of NO$_3$. A concentration of 0.78 mM NO$_3$ results in the longest nanorods of all five cases. This implies that there is an optimal concentration of NO$_3$ which results in long gold nanorods even if the growth solution becomes a gel.

The number of seeds in the growth solution was also examined. Smaller amounts of seeds in the growth solution have been reported to result in longer gold nanorods.[19,39] Therefore the resulting length of the nanorods was examined as function of the number of seeds in the growth solution. The number of seeds was changed in two different ways. In method

(1), the number density of the seeds in the seed suspension were changed accompanied with the change in the amount of reducing agents used to organize the seeds. In this case, the same amount of seed suspension was added to the growth solutions. In method (2), different amounts of the same seed suspension was added to the growth solutions.
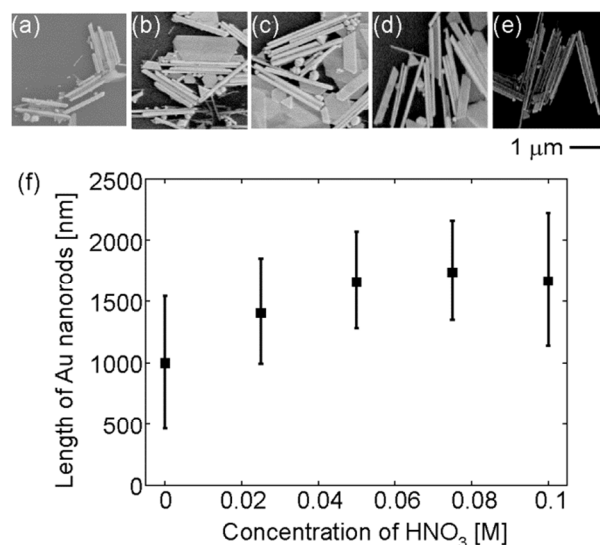

Figure 2. SEM images of gold nanorods grown with (a) 0 mM, (b) 0.26 mM, (c) 0.52 mM, (d) 0.78 mM, and (e) 1.0 mM of NO$_3$. (f) Average length and standard deviation of resulting gold nanorods shown in (a)-(e).

The results from method (1) will be discussed first. As previously stated, in this method, the number density of seeds in the seed suspension was changed. It means that the number of seeds added to the growth solution was changed. The number of seeds can be estimated from both the concentration of Au ions in the seed solution and the size of the seeds (which was measured using dynamic light scattering (DLS: Zetasizer Nano ZEN3600, Malvern)). Since the concentration of Au ions in all the seed solutions are the same, the number density of the seeds was changed by modifying the seed size which, in turn, was modified by changing the amount of reducing agent, i.e., the concentration of NaBH$_4$ in the citric acid solution. Four concentrations (2, 10, 50, and 100 mM) of NaBH$_4$ were used. Furthermore, the seed size was measured just 2 h after preparing the seed suspension. The DLS-measured average seed sizes are 4.6, 3.4, 3.5, and 5.8 nm for concentrations of NaBH$_4$ in citrate acid solution of 2, 10, 50, and 100 mM, respectively. The average size of seeds, shown in Figure 3 does not change significantly with changing concentrations of NaBH$_4$.

Here we should note the concentration of NaBH$_4$ used for making seeds. Nanorods have been grown with concentrations of 10 mM[10,12] and 100 mM[16,39-42] of NaBH$_4$ in previous investigations. However the seed suspension that contains 100 mM NaBH$_4$ gradually changes color (data are not shown) and seems to be unstable. On the other hand, the seed suspension with 10 or 50 mM NaBH$_4$ does not change color and appears to be stable. Moreover, as Murphy et al. proposed,[17] the small sizes and corresponding narrow size distribution of the seeds with 10 or 50 mM NaBH$_4$ might contribute to the stability of these seeds.

The number of seeds will be estimated from the seed size as follows. For simplicity, the distance between the Au atoms in

the seed crystal is set to 4 Å, and each seed made with 2, 10, 50, and 100 mM NaBH$_4$ is designated as a cube with side dimensions of 4.6, 3.4, 3.5, and 5.8 nm, respectively. If the Au concentration in a seed solution, all of which are assumed to be used for making seeds, is taken into consideration, then the resulting numbers of seeds are $\sim 1.5 \times 10^{12}$, $\sim 3.5 \times 10^{12}$, $\sim 3.5 \times 10^{12}$ and $\sim 7.5 \times 10^{11}$ for NaBH$_4$ concentrations of 2, 10, 50 and 100 mM, respectively.
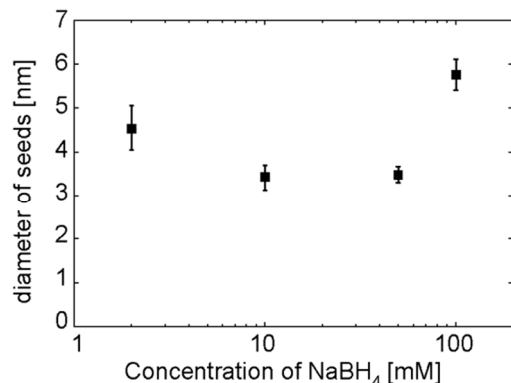

Figure 3. The DLS-measured sizes of seeds which were made with different concentrations of NaBH$_4$.
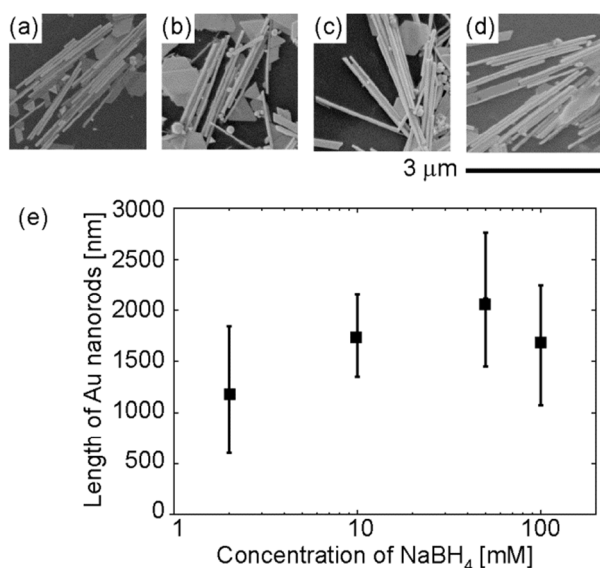

Figure 4. Gold nanorods grown with the seeds in Fig. 3. SEM images of gold nanorods with the seeds which were made of (a) 2 mM, (b) 10 mM, (c) 50 mM and (d) 100 mM NaBH$_4$. (e) Average length and standard deviation of resulting gold nanorods shown in (a)-(d).

The resulting length of nanorods will be estimated from the number of the seeds. The same concentrations of Au ions were added to the growth solutions. It is assumed that all of the Au ions are involved in making the nanorods and that they are equally distributed to each seed. As such, the lengths of the gold nanorods with seeds of 10 or 50 mM NaBH$_4$ are expected to be shorter than those of the other two nanorods since the number of seed of the former are more than those of the latter (The nanorods were assigned similar diameters in each case, as shown in Fig. 4, i.e., $\sim$ 70 nm). However, the present results (Fig. 4e) show the opposite tendency; i.e., the nanorods with seeds of 10 or 50 mM NaBH$_4$ are longer than the other two

nanorods. From this result, the number of seeds in the gelled growth solution seems to have no effect on the length of the gold nanorods. We will confirm this result with method (2).

In method (2), the amount of seed suspension made from 10 mM NaBH$_4$ was varied in order to determine the effect of the number of seeds on the length of the nanorods. Different amounts (3.2, 17, and 85 μl) of this seed were added to the growth solutions. The results in Fig. 5 and Table S3 revealed that the lengths of the nanorods do not change significantly when the amount of seeds is varied. The lengths of the nanorods, in contrast, changed significantly with changes in the number of seeds (Fig. S1, Table S4) when the parameters are all the same, except for the gelation of the growth solution. Therefore, the gelation has a stronger effect on the length of the nanorods than the difference in the number of seeds.

In previous investigations, where the relation between the number of seeds and the length of nanorods was studied, the gold nanorods grew in the surfactant solution with a micellar structure.[19,24,39] On the contrary, in the present experiments, the gold nanorods grow in the surfactant solution with a lamellar structure. In the present case, long nanorods with lengths of over 1 μm grow possibly as a result of the higher stability of the complex between the Au ions and the lamellar structure compared to that of the micellar structure despite the difference in the number of seeds.[19] However, details of the mechanism that governs the elongation of nanorods in the lamellar structure remain unclear and will be explored in future studies.
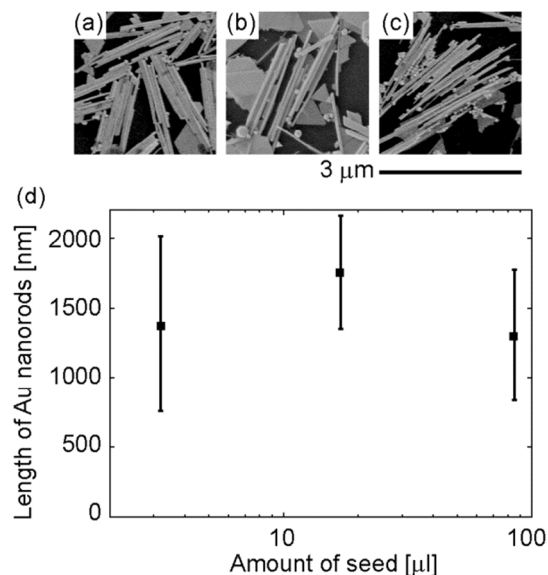

Figure 5. Gold nanorods grown at 20 °C with different amounts of the same seed. SEM images of the nanorods with (a) 3.2 μl, (b) 17 μl, and (c) 85 μl of the same seeds. (d) Average length and standard deviation of the nanorods shown in (a)-(c).

Tables S2 and S3 reveal that low yields of nanorods were obtained in this investigation. At first glance, the simple comparison between the number of seeds and the length of the nanorods appears to be impossible owing to these low yields. In other words, except for those which became nanorods, many of the seeds grew to become nanoparticles, and it seemed that the average length of the gold nanorods could not be obtained from the number of equally-distributed Au ions per seed. However, a remarkable difference in the length of the nanorods with changing number of seeds was observed even at low yields (Fig. S1, Table S4). Therefore, insignificant differences in the

lengths with varying numbers of seeds (Fig. 5) cannot be attributed to the low yields of these nanorods.

The effects of the pH of the growth solution on the length of the twin gold nanorods were also examined. Busbee et al. studied the growth of gold nanorods with citrate-stabilized seeds, using a 3 step' method, by changing the pH of the growth solution.[40] They showed that higher yields of longer gold nanorods were obtained in a high pH solution (pH = 5.6) than in the case of low pH (pH = 3.5). The pH of the growth solution containing citrate-stabilized seeds and NO_3, and that of the growth solution using surfactant-stabilized seeds without NO_3 were 2.8 and 3.7 in the case of the present experiments and a previous study, respectively. Although, as expected, the yield of nanorods was higher in the previous system than in the present one, longer nanorods were obtained in the present study than in the previous study. The effect of only the pH is difficult, since NO_3 and citrate-stabilized seeds, both of which were also added to the growth solution in the present case, resulted in a slight change in the pH.

Conclusions

High-aspect-ratio twin gold nanorods with lengths of over 1000 nm can grow with citrate-stabilized seeds in one-pot synthesis using a gelled surfactant solution. The yield was around 60 % and the average length was 1755 nm. Although the previous methods of making long twin gold nanorods require at least 3 steps, this one-pot synthesis can be performed simply, without any complex procedures. The growth mechanisms of the current long twin nanorods, with lengths of over 1 μm, were compared to those reported in previous studies. The effect of pH is difficult to distinguish since many factors, including NO_3 added, affects the pH of the solution. NO_3 has an influence on the length of the gold nanorods and the longest ones were obtained at an optimal concentration of NO_3, even for growth in the gelled surfactant solution as well as the growth in aqueous surfactant solution. On the contrary, the number of seeds in the growth solution has no effect on the lengths of the nanorods. This stems possibly from the gelation of the growth solution and not from the stabilization of the seeds by the citrate. However, details of the mechanism governing the elongation of the nanorods in the lamellar structure remain unclear and will be explored in future studies.

Acknowledgements

Notes and references

a Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1, Higashi, Tsukuba 305-8565 Japan.
b PRESTO, JST, 4-1-8 Hon-cho, Kawaguchi, Saitama 332-0012, Japan.
† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1   A. Mieszawska, R. Jalilian, G.U. Sumanasekera, F.P. Zamborini, *J. Am. Chem. Soc.*, 2005, **127**, 10822.

2   Q. Tang, Y. Tong, T. Jain, T. Hassenkam, Q. Wan, K. Moth-Poulsen, T. Bjornholm, *Nanotechnology*, 2009, **20**, 245205.

3   T. Jain, F. Westerlund, E. Johnson, K. Moth-Poulsen, T. Bjornholm, *ACS Nano*, 2009, **3**, 828.

4   N. Taub, O. Krichevski, G. Markovich, *J. Phys. Chem. B*, 2003, **107**, 11579.

5   Z. Wei, A. J. Mieszawski, F. P. Zamborini, *Langmuir*, 2004, **20**, 4322.

6   Z. Wei, F. P. Zamborini, *Langmuir*, 2004, **20**, 11301.

7   A. J. Mieszawski, G. W. Slawinski, F. P. Zamborini, *J. Am. Chem. Soc.*, 2006, **128**, 5622.

8   Z.-K. Zhou, X.-N. Peng, Z.-J. Yang, Z.-S. Zhang, M. Li, X.-R. Su, Q. Zhang, X. Shan, Q. Wang, Z. Zhang, *Nano Lett.*, 2011, **11**, 49.

9   N. Yu, P. Genevet, M. A. Kats, F. Aieta, J.-P. Tetienne, F. Capasso, Z. Gaburro, *Science*, 2011, **334**, 333.

10 N. R. Jana, L. Gearheart, C. J. Murphy, *Adv. Mater.*, 2001, **13**, 1389.

11 D. K. Smith, N. R. Miller, B. A. Korgel, *Lagmuir*, 2009, **24**, 9518.

12 H.-Y. Wu, H.-C. Chu, T.-J. Kuo, C.-L. Kuo, M. H. Huang, *Chem. Mater.*, 2005, **17**, 6447.

13 H. M. Chen, H.-C. Peng, R.-S. Liu, K. Asakura, C.L. Lee, J.F. Lee, S.-F. Hu, *J. Phys. Chem. B*, 2005, **109**, 19553.

14 K. Critchley, B. P. Khanal, M. L. Gorzny, L. Vigderman, S. D. Evans, E. R. Zubarev, N. A. Kotov, *Adv. Mater.*, 2010, **22**, 2338.

15 Y. Takenaka, H. Kitahata, *Chem. Phys. Lett.*, 2009, **467**, 327.

16 A. Gole, C. J. Murphy, *Chem. Mater.*, 2004, **16**, 3633.

17 C. J. Murphy, L. B. Thompson, D. J. Chernak, J. A. Yang, S. T. Sivapalan, S. P. Boulos, J. Huang, A. M. Alkilany, P. N. Sisco, *Curr. Opin. Colloid Interface Sci.*, 2011, **16**, 128.

18 This mixture of the surfactants was used because of the following two reasons. First, surfactants should be cationic to bind anionic Au ions. It is known that the complex consisting of surfactant micelles and Au ions has an important role to elongate gold nanorods.[19,20] Second, surfactants should perform a coagel structure (a periodic structure of solid bilayer membranes separated by water layers) to synthesize long gold nanorods in a surfactant gel state as explained later.[15,19] The surfactants to satisfy the above two conditions are, for instance, those which have a head of trymethylammoniumbromide and a tail of an alkyl chain, where the number of carbon is 18.[21-23] Here, it should be noted that gold nanorods commonly grow well in a solution of HTAB.[10,11] Actually, long gold nanorods grow from surfactant-stabilized seeds in a mixed surfactant solution of HTAB and OTAB.[15] Thus the mixture of HTAB and OTAB was used as a surfactant solution.

19 Y. Takenaka, Y. Kawabata, H. Kitahata, M. Yoshida, Y. Matsuzawa, T. Ohzono, *J. Colloid Interface Sci.*, 2013, **407**, 265.

20 J. Perez-Juste, L. M. Liz-Marzan, S. Carnie, D. Y. C. Chan. P. Mulvaney, *Adv. Funct. Mater.*, 2004, **14**, 571.

21 S. Si, C. Leduc, M.-H. Delville, B. Lounis, *Chem. Phys. Chem.*, 2012, **13**, 193.

22 M. Kodama, K. Tsujii, S. Seki, *J. Phys. Chem.*, 1990, **94**, 815.

23 M. Kodama, S. Seki, *Adv. Colloid Interface Sci.*, 1991, **35**, 1.

24 Y. Takenaka, H. Kitahata, *Phys. Rev. E*, 2009, **80**, 020601(R).

25 I. Rico, A. Lattes, *J. Phys. Chem.*, 1986, **90**, 5870.

26 M. Tsuchiya, K. Tsujii, K. Maki, T. Tanaka, *J. Phys. Chem.*, 1994, **98**, 6187.

27 C. J. Johnson, E. Dujardin, S. A. Davis, C. J. Murphy, S. Mann, *J. Mater. Chem.*, 2002, **12**, 1765.

28 P. L. Gai, M. A. Harmer, *Nano Lett.*, 2002, **2**, 771.

29 H.-C. Chu, C.-H. Kuo, M. H. Huang, *Inorg. Chem.*, 2006, **45**, 808.

30 H.-Y. Wu, W.-L. Huang, M. H. Huang, *Cryst. Growth Des.*, 2007, **7**, 831.

31 X. Huang, S. Neretina, M. A. El-Sayed, *Adv. Mater.*, 2009, **21**, 4880.

32 V. Sharma, K. Park, M. Srinivasarao, *Mater. Sci. Eng. R*, 2009, **65**, 1.

33 T. H. Ha, H.-J. Koo, B. H. Chung, *J. Phys. Chem. C*, 2007, **111**, 1123.

34 D. K. Smith, B. A. Korgel, *Langmuir*, 2008, **24**, 644.

35 Y. Takenaka, Y. Kawabata, H. Kitahata, T. Ohzono, *Chem. Lett.*. 2012, **41**, 1173.

36 Y. Takenaka, h. Kitahata, N. L. Yamada, H. Seto, M. Hara, *J. Colloid Interface Sci.*, 2011, **356**, 111.

37 N. R. Jana, *Small*, 2005, **1**, 875.

38 M. S. Bakshi, F. Possmayer, N. O. Petersen, *J. Phys. Chem. C*, 2008, **112**, 8259.

39 C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi, T. Li, *J. Phys. Chem. B*, 2005, **109**, 13857.

40 B. D. Busbee, S. O. Obare, C. J. Murphy, *Adv. Mater.*, 2003, **15**, 414.

41 N. R. Jana, L. Gearheart, C. J. Murphy, *J. Phys. Chem. B*, 2001, **105**, 4065.

42 H. J. Park, C. S. Ah, W.-J. Kim, I. S. Choi, K.-P. Lee, W. S. Yun, *J. Vac. Sci. Technol. A,* 2006, **24**, 1323.